Section IV

ORGANIC MOLECULAR FUNCTIONAL GROUPS AND MOLECULES

Organic molecules comprising an arbitrary number of atoms can be solved using the similar principles and procedures as those used to solve alkanes of arbitrary length. Alkanes can be considered to be comprised of the functional groups of CH_3, CH_2, and $C-C$. These groups with the corresponding geometrical parameters and energies can be added as a linear sum to give the solution of any straight chain alkane as shown in the Continuous-Chain Alkanes section. Similarly, the geometrical parameters and energies of all functional groups such as alkanes, branched alkanes, alkenes, branched alkenes, alkynes, alkyl fluorides, alkyl chlorides, alkyl bromides, alkyl iodides, alkene halides, primary alcohols, secondary alcohols, tertiary alcohols, ethers, primary amines, secondary amines, tertiary amines, aldehydes, ketones, carboxylic acids, carboxylic esters, amides, N-alkyl amides, N,N-dialkyl amides, urea, acid halides, acid anhydrides, nitriles, thiols, sulfides, disulfides, sulfoxides, sulfones, sulfites, sulfates, nitro alkanes, nitrites, nitrates, conjugated polyenes, aromatics, heterocyclic aromatics, substituted aromatics, and others can be solved. The functional-group solutions can be made into a linear superposition and sum, respectively, to give the solution of any organic molecule. The solutions of the functional groups can be conveniently obtained by using generalized forms of the geometrical and energy equations. The equations and sections that are referenced by not contained in this text refer to those sections and equations of the book by R. L. Mills entitled, "The Grand Unified Theory of Classical Quantum Mechanics", June 2006 Edition, Cadmus Professional Communications-Science Press Division, Ephrata, PA, ISBN 0963517171, Library of Congress Control Number 2005936834; posted at **http://www.blacklightpower.com/bookdownload.shtml** which is incorporated in its entirety by reference.

Consider the case wherein at least two atomic orbital hybridize as a linear combination of electrons at the same energy in order to achieve a bond at an energy minimum, and the sharing of electrons between two or more such orbitals to form a MO permits the participating hybridized orbitals to decrease in energy through a decrease in the radius of one or more of the participating orbitals. The force generalized constant k' of a

H_2-type ellipsoidal MO due to the equivalent of two point charges of at the foci is given by:

$$k' = \frac{C_1C_2 2e^2}{4\pi\varepsilon_0} \tag{15.1}$$

where C_1 is the fraction of the H_2-type ellipsoidal MO basis function of a chemical bond of the molecule or molecular ion which is 0.75 (Eq. (13.59)) in the case of H bonding to a central atom and 0.5 (Eq. (14.152)) otherwise, and C_2 is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of the chemical bond. From Eqs. (13.58-13.63), the distance from the origin of the MO to each focus c' is given by:

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2C_1C_2 a}} = \sqrt{\frac{aa_0}{2C_1C_2}} \tag{15.2}$$

The internuclear distance is

$$2c' = 2\sqrt{\frac{aa_0}{2C_1C_2}} \tag{15.3}$$

The length of the semiminor axis of the prolate spheroidal MO $b = c$ is given by

$$b = \sqrt{a^2 - c'^2} \tag{15.4}$$

And, the eccentricity, e, is

$$e = \frac{c'}{a} \tag{15.5}$$

From Eqs. (11.207-11.212), the potential energy of the two electrons in the central field of the nuclei at the foci is

$$V_e = n_1 c_1 c_2 \frac{-2e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{15.6}$$

The potential energy of the two nuclei is

$$V_p = n_1 \frac{e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}} \tag{15.7}$$

The kinetic energy of the electrons is

$$T = n_1 c_1 c_2 \frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{15.8}$$

And, the energy, V_m, of the magnetic force between the electrons is

$$V_m = n_1 c_1 c_2 \frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{15.9}$$

The total energy of the H_2-type prolate spheroidal MO, $E_T(H_2MO)$, is given by the sum of the energy terms:

$$E_T(H_2MO) = V_e + T + V_m + V_p \tag{15.10}$$

$$\begin{aligned} E_T(H_2MO) &= -\frac{n_1 e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}}\left[c_1 c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} - 1\right] \\ &= -\frac{n_1 e^2}{8\pi\varepsilon_0 c'}\left[c_1 c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'} - 1\right] \end{aligned} \tag{15.11}$$

where n_1 is the number of equivalent bonds of the MO and applies in the case of functional groups. In the case of independent MOs not in contact with the bonding atoms, the terms based on charge are multiplied by c_{BO}, the bond-order factor. It is 1 for a single bond, 4 for an independent double bond as in the case of the CO_2 and NO_2 molecules, and 9 for an independent triplet bond. Then, the kinetic energy term is multiplied by c'_{BO} which is 1 for a single bond, 2 for a double bond, and 9/2 for a triple bond. c_1 is the fraction of the H_2-type ellipsoidal MO basis function of an MO which is 0.75 (Eqs. (13.67-13.73)) in the case of H bonding to an unhybridized central atom and 1 otherwise, and c_2 is the factor that results in an equipotential energy match of the participating the MO and the at least two atomic orbitals of the chemical bond. Specifically, to meet the equipotential condition and energy matching conditions for the union of the H_2-type-ellipsoidal-MO and the HOs or AOs of the bonding atoms, the factor c_2 of a H_2-type ellipsoidal MO may given by (i) one, (ii) the ratio of the Coulombic or valence energy of the AO or HO of at least one atom of the bond and 13.605804 eV, the Coulombic energy between the electron and proton of H, (iii) the ratio of the valence energy of the AO or HO of one atom and the Coulombic energy of another, (iv) the ratio of the valence energies of the AOs or HOs of two atoms, (v) the ratio of two c_2 factors corresponding to any of cases (ii)-(iv), and (vi) the product of two different c_2 factors corresponding to any of the cases (i)-(v). Specific examples of the factor c_2 of a H_2-type ellipsoidal MO given in previous sections are

0.936127, the ratio of the ionization energy of N 14.53414 eV and 13.605804 eV, the Coulombic energy between the electron and proton of H;

0.91771, the ratio of $14.82575\ eV$, $-E_{Coulomb}\left(C,2sp^3\right)$, and $13.605804\ eV$;

0.87495, the ratio of $15.55033\ eV$, $-E_{Coulomb}\left(C_{ethane},2sp^3\right)$, and $13.605804\ eV$;

0.85252, the ratio of $15.95955\ eV$, $-E_{Coulomb}\left(C_{ethylene},2sp^3\right)$, and $13.605804\ eV$;

0.85252, the ratio of $15.95955\ eV$, $-E_{Coulomb}\left(C_{benzene},2sp^3\right)$, and $13.605804\ eV$, and

0.86359, the ratio of $15.55033\ eV$, $-E_{Coulomb}\left(C_{alkane},2sp^3\right)$, and $13.605804\ eV$.

In the generalization of the hybridization of at least two atomic-orbital shells to form a shell of hybrid orbitals, the hybridized shell comprises a linear combination of the electrons of the atomic-orbital shells. The radius of the hybridized shell is calculated from the total Coulombic energy equation by considering that the central field decreases by an integer for each successive electron of the shell and that the total energy of the shell is equal to the total Coulombic energy of the initial AO electrons. The total energy $E_T\left(atom,msp^3\right)$ (m is the integer of the valence shell) of the AO electrons and the hybridized shell is given by the sum of energies of successive ions of the atom over the n electrons comprising total electrons of the at least one AO shell.

$$E_T\left(atom,msp^3\right)=-\sum_{m=1}^{n} IP_m \tag{15.12}$$

where IP_m is the mth ionization energy (positive) of the atom. The radius r_{msp^3} of the hybridized shell is given by:

$$r_{msp^3}=\sum_{q=Z-n}^{Z-1}\frac{-(Z-q)e^2}{8\pi\varepsilon_0 E_T\left(atom,msp^3\right)} \tag{15.13}$$

Then, the Coulombic energy $E_{Coulomb}\left(atom,msp^3\right)$ of the outer electron of the $atom\ msp^3$ shell is given by

$$E_{Coulomb}\left(atom,msp^3\right)=\frac{-e^2}{8\pi\varepsilon_0 r_{msp^3}} \tag{15.14}$$

In the case that during hybridization at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy $E(magnetic)$ at the initial radius r of the AO electron:

$$E(magnetic)=\frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 r^3}=\frac{8\pi\mu_o\mu_B^2}{r^3} \tag{15.15}$$

Then, the energy $E\left(atom,msp^3\right)$ of the outer electron of the *atom msp*^{3} shell is given by the sum of $E_{Coulomb}\left(atom,msp^3\right)$ and $E(magnetic)$:

$$E\left(atom,msp^3\right) = \frac{-e^2}{8\pi\varepsilon_0 r_{msp^3}} + \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 r^3} \tag{15.16}$$

Consider next that the at least two atomic orbitals hybridize as a linear combination of electrons at the same energy in order to achieve a bond at an energy minimum with another atomic orbital or hybridized orbital. As a further generalization of the basis of the stability of the MO, the sharing of electrons between two or more such hybridized orbitals to form a MO permits the participating hybridized orbitals to decrease in energy through a decrease in the radius of one or more of the participating orbitals. In this case, the total energy of the hybridized orbitals is given by the sum of $E\left(atom,msp^3\right)$ and the next energies of successive ions of the atom over the n electrons comprising the total electrons of the at least two initial AO shells. Here, $E\left(atom,msp^3\right)$ is the sum of the first ionization energy of the atom and the hybridization energy. An example of $E\left(atom,msp^3\right)$ for $E\left(C,2sp^3\right)$ is given in Eq. (14.503) where the sum of the negative of the first ionization energy of C, $-11.27671\ eV$, plus the hybridization energy to form the $C2sp^3$ shell given by Eq. (14.146) is $E\left(C,2sp^3\right) = -14.63489\ eV$.

Thus, the sharing of electrons between two *atom msp*^{3} HOs to form an atom-atom-bond MO permits each participating hybridized orbital to decrease in radius and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, each *atom msp*^{3} HO donates an excess of 25% per bond of its electron density to the atom-atom-bond MO to form an energy minimum wherein the atom-atom bond comprises one of a single, double, or triple bond. In each case, the radius of the hybridized shell is calculated from the Coulombic energy equation by considering that the central field decreases by an integer for each successive electron of the shell and the total energy of the shell is equal to the total Coulombic energy of the initial AO electrons plus the hybridization energy. The total energy $E_T\left(mol.atom,msp^3\right)$ (m is the integer of the valence shell) of the HO electrons is given by the sum of energies of successive ions of the atom over the n electrons comprising total electrons of the at least one initial AO shell and the hybridization energy:

$$E_T\left(mol.atom,msp^3\right)=E\left(atom,msp^3\right)-\sum_{m=2}^{n}IP_m \tag{15.17}$$

where IP_m is the mth ionization energy (positive) of the atom and the sum of $-IP_1$ plus the hybridization energy is $E\left(atom,msp^3\right)$. Thus, the radius r_{msp^3} of the hybridized shell is given by:

$$r_{msp^3}=\left(\sum_{q=Z-n}^{Z-1}(Z-q)-s(0.25)\right)\frac{-e^2}{8\pi\varepsilon_0 E_T\left(mol.atom,msp^3\right)} \tag{15.18}$$

where $s=1,2,3$ for a single, double, and triple bond, respectively. The Coulombic energy $E_{Coulomb}\left(mol.atom,msp^3\right)$ of the outer electron of the *atom* msp^3 shell is given by

$$E_{Coulomb}\left(mol.atom,msp^3\right)=\frac{-e^2}{8\pi\varepsilon_0 r_{msp^3}} \tag{15.19}$$

In the case that during hybridization at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy $E(magnetic)$ at the initial radius r of the AO electron given by Eq. (15.15). Then, the energy $E\left(mol.atom,msp^3\right)$ of the outer electron of the *atom* msp^3 shell is given by the sum of $E_{Coulomb}\left(mol.atom,msp^3\right)$ and $E(magnetic)$:

$$E\left(mol.atom,msp^3\right)=\frac{-e^2}{8\pi\varepsilon_0 r_{msp^3}}+\frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 r^3} \tag{15.20}$$

$E_T\left(atom-atom,msp^3\right)$, the energy change of each *atom* msp^3 shell with the formation of the atom-atom-bond MO is given by the difference between $E\left(mol.atom,msp^3\right)$ and $E\left(atom,msp^3\right)$:

$$E_T\left(atom-atom,msp^3\right)=E\left(mol.atom,msp^3\right)-E\left(atom,msp^3\right) \tag{15.21}$$

As examples from prior sections, $E_{Coulomb}\left(mol.atom,msp^3\right)$ is one of:

$E_{Coulomb}\left(C_{ethylene},2sp^3\right)$, $E_{Coulomb}\left(C_{ethane},2sp^3\right)$, $E_{Coulomb}\left(C_{acetylene},2sp^3\right)$, and $E_{Coulomb}\left(C_{alkane},2sp^3\right)$;

$E_{Coulomb}\left(atom,msp^3\right)$ is one of $E_{Coulomb}\left(C,2sp^3\right)$ and $E_{Coulomb}\left(Cl,3sp^3\right)$;

$E(mol.atom,msp^3)$ is one of $E(C_{ethylene},2sp^3)$, $E(C_{ethane},2sp^3)$, $E(C_{acetylene},2sp^3)\,E(C_{alkane},2sp^3)$;

$E(atom,msp^3)$ is one of and $E(C,2sp^3)$ and $E(Cl,3sp^3)$;

$E_T(atom-atom,msp^3)$ is one of $E(C-C,2sp^3)$, $E(C=C,2sp^3)$, and. $E(C\equiv C,2sp^3)$;

$atom\ msp^3$ is one of $C2sp^3$, $Cl3sp^3$

$E_T(atom-atom(s_1),msp^3)$ is $E_T(C-C,2sp^3)$ and $E_T(atom-atom(s_2),msp^3)$ is $E_T(C=C,2sp^3)$, and

r_{msp^3} is one of r_{C2sp^3}, $r_{ethane2sp^3}$, $r_{ethylene2sp^3}$, $r_{acetylene2sp^3}$, $r_{alkane2sp^3}$, and r_{Cl3sp^3}.

In the case of the $C2sp^3$ HO, the initial parameters (Eqs. (14.142-14.146)) are

$$r_{2sp^3}=\sum_{n=2}^{5}\frac{(Z-n)e^2}{8\pi\varepsilon_0(e148.25751\ eV)}=\frac{10e^2}{8\pi\varepsilon_0(e148.25751\ eV)}=0.91771a_0 \tag{15.22}$$

$$E_{Coulomb}(C,2sp^3)=\frac{-e^2}{8\pi\varepsilon_0 r_{2sp^3}}=\frac{-e^2}{8\pi\varepsilon_0 0.91771a_0}=-14.82575\ eV \tag{15.23}$$

$$E(magnetic)=\frac{2\pi\mu_0 e^2\hbar^2}{m_e^2(r_3)^3}=\frac{8\pi\mu_o\mu_B^2}{(0.84317a_0)^3}=0.19086\ eV \tag{15.24}$$

$$\begin{aligned}E(C,2sp^3)&=\frac{-e^2}{8\pi\varepsilon_0 r_{2sp^3}}+\frac{2\pi\mu_0 e^2\hbar^2}{m_e^2(r_3)^3}\\&=-14.82575\ eV+0.19086\ eV\\&=-14.63489\ eV\end{aligned} \tag{15.25}$$

In Eq. (15.18),

$$\sum_{q=Z-n}^{Z-1}(Z-q)=10 \tag{15.26}$$

Eqs. (14.147) and (15.17) give

$$E_T(mol.atom,msp^3)=E_T(C_{ethane},2sp^3)=-151.61569\ eV \tag{15.27}$$

Using Eqs. (15.18-15.28), the final values of r_{C2sp^3}, $E_{Coulomb}(C2sp^3)$, and $E(C2sp^3)$, and the resulting $E_T\left(C\overset{BO}{-}C,C2sp^3\right)$ of the MO due to charge donation from the HO to the MO where

$\overset{BO}{C-C}$ refers to the bond order of the carbon-carbon bond for different values of the parameter s are given in Table 15.1.

Table 15.1. The final values of r_{C2sp^3}, $E_{Coulomb}(C2sp^3)$, and $E(C2sp^3)$ and the resulting $E_T\left(\overset{BO}{C-C},C2sp^3\right)$ of the MO due to charge donation from the HO to the MO where $\overset{BO}{C-C}$ refers to the bond order of the carbon-carbon bond.

MO Bond Order (BO)	s 1	s 2	$r_{C2sp^3}(a_0)$ Final	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	$E_T\left(\overset{BO}{C-C},C2sp^3\right)$ (eV)
I	1	0	0.87495	-15.55033	-15.35946	-0.72457
II	2	0	0.85252	-15.95955	-15.76868	-1.13379
III	3	0	0.83008	-16.39089	-16.20002	-1.56513
IV	4	0	0.80765	-16.84619	-16.65532	-2.02043

In another generalized case of the basis of forming a minimum-energy bond with the constraint that it must meet the energy matching condition for all MOs at all HOs or AOs, the energy $E(mol.atom,msp^3)$ of the outer electron of the *atom* msp^3 shell of each bonding atom must be the average of $E(mol.atom,msp^3)$ for two different values of s:

$$E(mol.atom,msp^3)=\frac{E(mol.atom(s_1),msp^3)+E(mol.atom(s_2),msp^3)}{2} \quad (15.28)$$

In this case, $E_T(atom-atom,msp^3)$, the energy change of each *atom* msp^3 shell with the formation of each atom-atom-bond MO, is average for two different values of s:

$$E_T(atom-atom,msp^3)=\frac{E_T(atom-atom(s_1),msp^3)+E_T(atom-atom(s_2),msp^3)}{2} \quad (15.29)$$

Consider an aromatic molecule such as benzene given in the Benzene Molecule section. Each $C=C$ double bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from two sets of two $C2sp^3$ HOs of the participating carbon atoms. Each $C-H$ bond of CH having two spin-paired electrons, one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom, comprises the

linear combination of 75% H_2-type ellipsoidal MO and 25% $C2sp^3$ HO as given by Eq. (13.439). However, $E_T\left(atom-atom,msp^3\right)$ of the $C-H$-bond MO is given by $0.5E_T\left(C=C,2sp^3\right)$ (Eq. (14.247)) corresponding to one half of a double bond that matches the condition for a single-bond order for $C-H$ that is lowered in energy due to the aromatic character of the bond.

A further general possibility is that a minimum-energy bond is achieved with satisfaction of the potential, kinetic, and orbital energy relationships by the formation of an MO comprising an allowed multiple of a linear combination of H_2-type ellipsoidal MOs and corresponding HOs or AOs that contribute a corresponding allowed multiple (e.g. 0.5, 0.75, 1) of the bond order given in Table 15.1. For example, the alkane MO given in the Continuous-Chain Alkanes section comprises a linear combination of factors of 0.5 of a single bond and 0.5 of a double bond.

Consider a first MO and its HOs comprising a linear combination of bond orders and a second MO that shares a HO with the first. In addition to the mutual HO, the second MO comprises another AO or HO having a single bond order or a mixed bond order. Then, in order for the two MOs to be energy matched, the bond order of the second MO and its HOs or its HO and AO is a linear combination of the terms corresponding to the bond order of the mutual HO and the bond order of the independent HO or AO. Then, in general, $E_T\left(atom-atom,msp^3\right)$, the energy change of each $atom\ msp^3$ shell with the formation of each atom-atom-bond MO, is a weighted linear sum for different values of s that matches the energy of the bonded MOs, HOs, and AOs:

$$E_T\left(atom-atom,msp^3\right)=\sum_{n=1}^{N} c_{s_n} E_T\left(atom-atom\left(s_n\right),msp^3\right) \tag{15.30}$$

where c_{s_n} is the multiple of the BO of s_n. The radius r_{msp^3} of the $atom\ msp^3$ shell of each bonding atom is given by the Coulombic energy using the initial energy $E_{Coulomb}\left(atom,msp^3\right)$ and $E_T\left(atom-atom,msp^3\right)$, the energy change of each $atom\ msp^3$ shell with the formation of each atom-atom-bond MO:

$$r_{msp^3}=\frac{-e^2}{8\pi\varepsilon_0 a_0\left(E_{Coulomb}\left(atom,msp^3\right)+E_T\left(atom-atom,msp^3\right)\right)} \tag{15.31}$$

where $E_{Coulomb}(C2sp^3) = -14.825751\ eV$. The Coulombic energy $E_{Coulomb}(mol.atom, msp^3)$ of the outer electron of the *atom* msp^3 shell is given by Eq. (15.19). In the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy $E(magnetic)$ (Eq. (15.15)) at the initial radius r of the AO electron. Then, the energy $E(mol.atom, msp^3)$ of the outer electron of the *atom* msp^3 shell is given by the sum of $E_{Coulomb}(mol.atom, msp^3)$ and $E(magnetic)$ (Eq. (15.20)). $E_T(atom-atom, msp^3)$, the energy change of each *atom* msp^3 shell with the formation of the atom-atom-bond MO is given by the difference between $E(mol.atom, msp^3)$ and $E(atom, msp^3)$ given by Eq. (15.21). Using Eq. (15.23) for $E_{Coulomb}(C,2sp^3)$ in Eq. (15.31), the single bond order energies given by Eqs. (15.18-15.27) and shown in Table 15.1, and the linear combination energies (Eqs. (15.28-15.30)), the parameters of linear combinations of bond orders and linear combinations of mixed bond orders are given in Table 15.2.

Table 15.2. The final values of r_{C2sp^3}, $E_{Coulomb}(C2sp^3)$, and $E(C2sp^3)$ and the resulting $E_T\left(C\overset{BO}{-}C, C2sp^3\right)$ of the MO comprising a linear combination of H_2-type ellipsoidal MOs and corresponding HOs of single or mixed bond order where c_{s_n} is the multiple of the bond order parameter $E_T(atom-atom(s_n), msp^3)$ given in Table 15.1.

Table 15.1

MO Bond Order (BO)	s_1	c_{s_1}	s_2	c_{s_2}	s_3	c_{s_3}	$r_{C2sp^3}(a_0)$ Final	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	$E_T\left(C\overset{BO}{-}C,C2sp^3\right)$ (eV)
1/2I	1	0.5	0	0	0	0	0.89582	-15.18804	-14.99717	-0.36228
1/2II	2	0.5	0	0	0	0	0.88392	-15.39265	-15.20178	-0.56689
I + 1/2II	1	0.5	2	0.25	0	0	0.87941	-15.47149	-15.28062	-0.64573
1/2II + (I + II)	2	0.25	1	0.25	2	0.25	0.87363	-15.57379	-15.38293	-0.74804
3/4II	2	0.75	0	0	0	0	0.86793	-15.67610	-15.48523	-0.85034
I + II	1	0.5	2	0.5	0	0	0.86359	-15.75493	-15.56407	-0.92918
I + III	1	0.5	3	0.5	0	0	0.85193	-15.97060	-15.77974	-1.14485
I + IV	1	0.5	4	0.5	0	0	0.83995	-16.19826	-16.00739	-1.37250
II + III	2	0.5	3	0.5	0	0	0.84115	-16.17521	-15.98435	-1.34946
II + IV	2	0.5	4	0.5	0	0	0.82948	-16.40286	-16.21200	-1.57711
III + IV	3	0.5	4	0.5	0	0	0.81871	-16.61853	-16.42767	-1.79278
IV + IV	4	0.5	4	0.5	0	0	0.80765	-16.84619	-16.65532	-2.02043

Consider next the radius of the AO or HO due to the contribution of charge to more than one bond. The energy contribution due to the charge donation at each atom such as carbon superimposes linearly. In general, the radius r_{mol2sp^3} of the $C2sp^3$ HO of a carbon atom of a given molecule is calculated using Eq. (14.514) by considering $\sum E_{T_{mol}}(MO,2sp^3)$, the total energy donation to each bond with which it participates in bonding. The general equation for the radius is given by

$$r_{mol2sp^3} = \frac{-e^2}{8\pi\varepsilon_0 \left(E_{Coulomb}\left(C,2sp^3\right) + \sum E_{T_{mol}}\left(MO,2sp^3\right)\right)} = \frac{e^2}{8\pi\varepsilon_0 \left(e14.825751\ eV + \sum \left|E_{T_{mol}}\left(MO,2sp^3\right)\right|\right)} \tag{15.32}$$

The Coulombic energy $E_{Coulomb}\left(mol.atom,msp^3\right)$ of the outer electron of the $atom\ msp^3$ shell is given by Eq. (15.19). In the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy $E(magnetic)$ (Eq. (15.15)) at the initial radius r of the AO electron. Then, the energy $E\left(mol.atom,msp^3\right)$ of the outer electron of the $atom\ msp^3$ shell is given by the sum of $E_{Coulomb}\left(mol.atom,msp^3\right)$ and $E(magnetic)$ (Eq. (15.20)).

For example, the $C2sp^3$ HO of each methyl group of an alkane contributes $-0.92918\ eV$ (Eq. (14.513)) to the corresponding single $C-C$ bond; thus, the corresponding $C2sp^3$ HO radius is given by Eq. (14.514). The $C2sp^3$ HO of each methylene group of C_nH_{2n+2} contributes $-0.92918\ eV$ to each of the two corresponding $C-C$ bond MOs. Thus, the radius (Eq. (15.32)), the Coulombic energy (Eq. (15.19)), and the energy (Eq. (15.20)) of each alkane methylene group are

$$\begin{aligned} r_{alkaneC_{methylene}2sp^3} &= \frac{-e^2}{8\pi\varepsilon_0 \left(E_{Coulomb}\left(C,2sp^3\right) + \sum E_{T_{alkane}}\left(methylene\ C-C,2sp^3\right)\right)} \\ &= \frac{e^2}{8\pi\varepsilon_0 \left(e14.825751\ eV + e0.92918\ eV + e0.92918\ eV\right)} \\ &= 0.81549a_0 \end{aligned} \tag{15.33}$$

$$E_{Coulomb}\left(C_{methylene}2sp^3\right) = \frac{-e^2}{8\pi\varepsilon_0 \left(0.81549a_0\right)} = -16.68412\ eV \tag{15.34}$$

$$E\left(C_{methylene}2sp^3\right) = \frac{-e^2}{8\pi\varepsilon_0 \left(0.81549a_0\right)} + \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(0.84317a_0\right)^3} = -16.49325\ eV \tag{15.35}$$

In the determination of the parameters of functional groups, heteroatoms bonding to $C2sp^3$ HOs to form MOs are energy matched to the $C2sp^3$ HOs. Thus, the radius and the energy parameters of a bonding heteroatom are given by the same equations as those for

$C2sp^3$ HOs. Using Eqs. (15.15), (15.19-15.20), (15.24), and (15.32) in a generalized fashion, the final values of the radius of the HO or AO, $r_{Atom.HO.AO}$, $E_{Coulomb}\left(mol.atom,msp^3\right)$, and $E\left(C_{mol}2sp^3\right)$ are calculated using $\sum E_{T_{group}}\left(MO,2sp^3\right)$, the total energy donation to each bond with which an atom participates in bonding corresponding to the values of $E_T\left(C\overset{BO}{-}C,C2sp^3\right)$ of the MO due to charge donation from the AO or HO to the MO given in Tables 15.1 and 15.2.

Table 15.3.A. The final values of $r_{Atom.HO.AO}$, $E_{Coulomb}\left(mol.atom,msp^3\right)$, and $E\left(C_{mol}2sp^3\right)$ calculated using the values of $E_T\left(C\overset{BO}{-}C,C2sp^3\right)$ given in Tables 15.1 and 15.2.

Atom Hybridization Designation	$E_T\left(\overset{BO}{C-C},C2sp^3\right)$	$E_T\left(\overset{BO}{C-C},C2sp^3\right)$	$E_T\left(\overset{BO}{C-C},C2sp^3\right)$	$E_T\left(\overset{BO}{C-C},C2sp^3\right)$	$E_T\left(\overset{BO}{C-C},C2sp^3\right)$	$r_{Atom.HO.AO}$ Final	$E_{Coulomb}(mol.atom,msp^3)$ (eV) Final	$E(C_{mol}2sp^3)$ (eV) Final
1	0	0	0	0	0	0.91771	-14.82575	-14.63489
2	-0.36229	0	0	0	0	0.89582	-15.18804	-14.99717
3	-0.46459	0	0	0	0	0.88983	-15.29034	-15.09948
4	-0.56689	0	0	0	0	0.88392	-15.39265	-15.20178
5	-0.72457	0	0	0	0	0.87495	-15.55033	-15.35946
6	-0.85034	0	0	0	0	0.86793	-15.6761	-15.48523
7	-0.92918	0	0	0	0	0.86359	-15.75493	-15.56407
8	-0.54343	-0.54343	0	0	0	0.85503	-15.91261	-15.72175
9	-1.13379	0	0	0	0	0.85252	-15.95955	-15.76868
10	-1.14485	0	0	0	0	0.85193	-15.9706	-15.77974
11	-0.46459	-0.82688	0	0	0	0.84418	-16.11722	-15.92636
12	-1.34946	0	0	0	0	0.84115	-16.17521	-15.98435
13	-1.3725	0	0	0	0	0.83995	-16.19826	-16.00739
14	-0.46459	-0.92918	0	0	0	0.83885	-16.21952	-16.02866
15	-0.72457	-0.72457	0	0	0	0.836	-16.2749	-16.08404
16	-0.5669	-0.92918	0	0	0	0.8336	-16.32183	-16.13097
17	-0.82688	-0.72457	0	0	0	0.83078	-16.37721	-16.18634
18	-1.56513	0	0	0	0	0.83008	-16.39089	-16.20002
19	-0.64574	-0.92918	0	0	0	0.82959	-16.40067	-16.20981
20	-1.57711	0	0	0	0	0.82948	-16.40286	-16.212
21	-0.72457	-0.92918	0	0	0	0.82562	-16.47951	-16.28865
22	-0.85035	-0.85035	0	0	0	0.82327	-16.52645	-16.33559
23	-1.79278	0	0	0	0	0.81871	-16.61853	-16.42767
24	-1.13379	-0.72457	0	0	0	0.81549	-16.68411	-16.49325
25	-0.92918	-0.92918	0	0	0	0.81549	-16.68412	-16.49325
26	-2.02043	0	0	0	0	0.80765	-16.84619	-16.65532

27	-1.13379	-0.92918	0	0	0	0.80561	-16.88872	-16.69786
28	-0.85035	-0.85035	-0.46459	0	0	0.80076	-16.99104	-16.80018
29	-0.5669	-0.72457	-0.92918	0	0	0.78916	-17.04641	-16.85554
30	-1.13379	-1.13379	0	0	0	0.79597	-17.09334	-16.90248
31	-1.34946	-0.92918	0	0	0	0.79546	-17.1044	-16.91353
32	-0.46459	-0.92918	-0.92918	0	0	0.79340	-17.14871	-16.95784
33	-0.64574	-0.85034	-0.85034	0	0	0.79232	-17.17217	-16.98131
34	-0.85035	-0.5669	-0.92918	0	0	0.79232	-17.17218	-16.98132
35	-0.72457	-0.72457	-0.92918	0	0	0.79085	-17.20408	-17.01322
36	-0.82688	-0.72457	-0.92918	0	0	0.78617	-17.30638	-17.11552
37	-0.72457	-0.92918	-0.92918	0	0	0.78155	-17.40868	-17.21782
38	-0.92918	-0.72457	-0.92918	0	0	0.78155	-17.40869	-17.21783
39	-0.54343	-0.54343	-0.5669	-0.92918	0	0.78155	-17.40869	-17.21783
40	-0.92918	-0.85034	-0.85034	0	0	0.77945	-17.45561	-17.26475
41	-0.82688	-0.92918	-0.92918	0	0	0.77699	-17.51099	-17.32013
42	-0.92918	-0.92918	-0.92918	0	0	0.77247	-17.6133	-17.42244
43	-0.85035	-0.54343	-0.5669	-0.92918	0	0.76801	-17.71561	-17.52475
44	-1.34946	-0.64574	-0.92918	0	0	0.76652	-17.75013	-17.55927
45	-0.85034	-0.54343	-0.60631	-0.92918	0	0.76631	-17.75502	-17.56415
46	-1.1338	-0.92918	-0.92918	0	0	0.7636	-17.81791	-17.62705
47	-0.46459	-0.85035	-0.85035	-0.92918	0	0.75924	-17.92022	-17.72936
48	-0.82688	-1.34946	-0.92918	0	0	0.75877	-17.93128	-17.74041
49	-1.13379	-1.13379	-1.13379	0	0	0.74646	-18.22712	-18.03626
50	-1.79278	-0.92918	-0.92918	0	0	0.73637	-18.47690	-18.28604

Table 15.3.B. The final values of $r_{Atom.HO.AO}$, $E_{Coulomb}\left(mol.atom,msp^3\right)$, and $E\left(C_{mol}2sp^3\right)$ calculated for heterocyclic groups using the values of $E_T\left(C\overset{BO}{-}C,C2sp^3\right)$ given in Tables 15.1 and 15.2.

Atom Hybridization Designation	$E_T\left(\overset{BO}{C-C},C2sp^3\right)$	$E_T\left(\overset{BO}{C-C},C2sp^3\right)$	$E_T\left(\overset{BO}{C-C},C2sp\right.$	$E_T\left(\overset{BO}{C-C},C2sp^3\right)$	$E_T\left(\overset{BO}{C-C},C2sp^3\right)$	$r_{Atom.HO.AO}$ Final	$E_{Coulomb}\left(mol.atom,msp^3\right)$ (eV) Final	$E\left(C_{mol}2sp^3\right)$ (eV) Final
1	0	0	0	0	0	0.91771	-14.82575	-14.63489
2	-0.56690	0	0	0	0	0.88392	-15.39265	-15.20178
3	-0.72457	0	0	0	0	0.87495	-15.55033	-15.35946
4	-0.92918	0	0	0	0	0.86359	-15.75493	-15.56407
5	-0.54343	-0.54343	0	0	0	0.85503	-15.91261	-15.72175
6	-1.13379	0	0	0	0	0.85252	-15.95954	-15.76868
7	-0.60631	-0.60631	0	0	0	0.84833	-16.03838	-15.84752
8	-0.46459	-0.92918	0	0	0	0.83885	-16.21953	-16.02866
9	-0.72457	-0.72457	0	0	0	0.83600	-16.27490	-16.08404
10	-0.92918	-0.60631	0	0	0	0.83159	-16.36125	-16.17038
11	-0.92918	-0.72457	0	0	0	0.82562	-16.47951	-16.28864
12	-0.85035	-0.85035	0	0	0	0.82327	-16.52644	-16.33558
13	-0.92918	-0.92918	0	0	0	0.81549	-16.68411	-16.49325
14	-1.13379	-0.72457	0	0	0	0.81549	-16.68412	-16.49325
15	-1.13379	-0.92918	0	0	0	0.80561	-16.88873	-16.69786
16	-0.85035	-0.85035	-0.46459	0	0	0.80076	-16.99103	-16.80017
17	-0.85034	-0.85034	-0.56690	0	0	0.79597	-17.09334	-16.90247
18	-1.13379	-1.13380	0	0	0	0.79597	-17.09334	-16.90248
19	-0.85035	-0.54343	0.00000	-0.92918	0	0.79340	-17.14871	-16.95785
20	-0.85035	-0.56690	-0.92918	0	0	0.79232	-17.17218	-16.98132
21	-0.54343	-0.54343	-0.56690	-0.92918	0	0.78155	-17.40869	-17.21783
22	-0.85034	-0.28345	-0.54343	-0.92918	0	0.78050	-17.43216	-17.24130
23	-0.92918	-0.92918	-0.92918	0	0	0.77247	-17.61330	-17.42243
24	-0.85034	-0.54343	-0.56690	-0.92918	0	0.76801	-17.71560	-17.52474
25	-0.85034	-0.54343	-0.60631	-0.92918	0	0.76631	-17.75502	-17.56416
26	-1.13379	-0.92918	-0.92918	0	0	0.76360	-17.81791	-17.62704

27	-1.13379	-1.13380	-0.72457	0	0	0.76360	-17.81791	-17.62705
28	-0.46459	-0.85035	-0.85035	-0.92918	0	0.75924	-17.92022	-17.72935
29	-1.13380	-1.13379	-0.92918	0	0	0.75493	-18.02252	-17.83166
30	-1.13379	-1.13379	-1.13379	0	0	0.74646	-18.22713	-18.03627

The energy of the MO is matched to each of the participating outermost atomic or hybridized orbitals of the bonding atoms wherein the energy match includes the energy contribution due to the AO or HO's donation of charge to the MO. The force constant k' (Eq. (15.1)) is used to determine the ellipsoidal parameter c' (Eq. (15.2)) of the each H_2-type-ellipsoidal-MO in terms of the central force of the foci. Then, c' is substituted into the energy equation (from Eq. (15.11))) which is set equal to n_1 times the total energy of H_2 where n_1 is the number of equivalent bonds of the MO and the energy of H_2, $-31.63536831\ eV$, Eq. (11.212) is the minimum energy possible for a prolate spheroidal MO. From the energy equation and the relationship between the axes, the dimensions of the MO are solved. The energy equation has the semimajor axis a as it only parameter. The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of each MO (Eqs. (15.3-15.5)). The parameter solutions then allow for the component and total energies of the MO to be determined.

The total energy, $E_T(H_2MO)$, is given by the sum of the energy terms (Eqs. (15.6-15.11)) plus $E_T(AO/HO)$:

$$E_T(H_2MO) = V_e + T + V_m + V_p + E_T(AO/HO) \tag{15.36}$$

$$\begin{aligned} E_T(H_2MO) &= -\frac{n_1 e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}}\left[c_1 c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}-1\right]+E_T(AO/HO) \\ &= -\frac{n_1 e^2}{8\pi\varepsilon_0 c'}\left[c_1 c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]+E_T(AO/HO) \end{aligned} \tag{15.37}$$

where n_1 is the number of equivalent bonds of the MO, c_1 is the fraction of the H_2-type ellipsoidal MO basis function of a chemical bond of the group, c_2 is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of each chemical bond, and $E_T(AO/HO)$ is the total energy comprising the difference of the energy $E(AO/HO)$ of at least one atomic or hybrid orbital to which the MO is energy matched and any energy component $\Delta E_{H_2MO}(AO/HO)$ due to the AO or HO's charge donation to the MO.

$$E_T(AO/HO) = E(AO/HO) - \Delta E_{H_2MO}(AO/HO) \tag{15.38}$$

As specific examples given in previous sections, $E_T(AO/HO)$ is one from the group of

$E_T(AO/HO) = E(O2p\ shell) = -E(ionization;\ O) = -13.6181\ eV$;

$E_T(AO/HO) = E(N2p\ shell) = -E(ionization;\ N) = -14.53414\ eV$;

$E_T(AO/HO) = E(C,2sp^3) = -14.63489\ eV$;

$E_T(AO/HO) = E_{Coulomb}(Cl,3sp^3) = -14.60295\ eV$;

$E_T(AO/HO) = E(ionization;\ C) + E(ionization;\ C^+)$;

$E_T(AO/HO) = E(C_{ethane},2sp^3) = -15.35946\ eV$;

$E_T(AO/HO) = +E(C_{ethylene},2sp^3) - E(C_{ethylene},2sp^3)$;

$E_T(AO/HO) = E(C,2sp^3) - 2E_T(C=C,2sp^3) = -14.63489\ eV - (-2.26758\ eV)$;

$E_T(AO/HO) = E(C_{acetylene},2sp^3) - E(C_{acetylene},2sp^3) - E(C_{acetylene},2sp^3) = 16.20002\ eV$;

$E_T(AO/HO) = E(C,2sp^3) - 2E_T(C\equiv C,2sp^3) = -14.63489\ eV - (-3.13026\ eV)$;

$E_T(AO/HO) = E(C_{benzene},2sp^3) - E(C_{benzene},2sp^3)$;

$E_T(AO/HO) = E(C,2sp^3) - E_T(C=C,2sp^3) = -14.63489\ eV - (-1.13379\ eV)$, and

$E_T(AO/HO) = E(C_{alkane},2sp^3) = -15.56407\ eV$.

To solve the bond parameters and energies, $c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2C_1C_2 a}} = \sqrt{\frac{aa_0}{2C_1C_2}}$ (Eq. (15.2)) is substituted into $E_T(H_2MO)$ to give

$$\begin{aligned}
E_T(H_2MO) &= -\frac{n_1 e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}}\left[c_1c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}-1\right]+E_T(AO/HO) \\
&= -\frac{n_1 e^2}{8\pi\varepsilon_0 c'}\left[c_1c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]+E_T(AO/HO) \qquad (15.39) \\
&= -\frac{n_1 e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2C_1C_2}}}\left[c_1c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2C_1C_2}}}{a-\sqrt{\frac{aa_0}{2C_1C_2}}}-1\right]+E_T(AO/HO)
\end{aligned}$$

The total energy is set equal to $E(basis\ energies)$ which in the most general case is given by

the sum of a first integer n_1 times the total energy of H_2 minus a second integer n_2 times the total energy of H, minus a third integer n_3 times the valence energy of $E(AO)$ (e.g. $E(N) = -14.53414\ eV$) where the first integer can be $1,2,3...$, and each of the second and third integers can be $0,1,2,3...$.

$$E(basis\ energies) = n_1(-31.63536831\ eV) - n_2(-13.605804\ eV) - n_3E(AO) \quad (15.40)$$

In the case that the MO bonds two atoms other than hydrogen, $E(basis\ energies)$ is n_1 times the total energy of H_2 where n_1 is the number of equivalent bonds of the MO and the energy of H_2, $-31.63536831\ eV$, Eq. (11.212) is the minimum energy possible for a prolate spheroidal MO:

$$E(basis\ energies) = n_1(-31.63536831\ eV) \quad (15.41)$$

$E_T(H_2MO)$, is set equal to $E(basis\ energies)$, and the semimajor axis a is solved. Thus, the semimajor axis a is solved from the equation of the form:

$$-\frac{n_1e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2C_1C_2}}}\left[c_1c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2C_1C_2}}}{a-\sqrt{\frac{aa_0}{2C_1C_2}}}-1\right] + E_T(AO/HO) = E(basis\ energies) \quad (15.42)$$

The distance from the origin of the H_2-type-ellipsoidal-MO to each focus c', the internuclear distance $2c'$, and the length of the semiminor axis of the prolate spheroidal H_2-type MO $b = c$ are solved from the semimajor axis a using Eqs. (15.2-15.4). Then, the component energies are given by Eqs. (15.6-15.9) and (15.39).

The total energy of the MO of the functional group, $E_T(MO)$, is the sum of the total energy of the components comprising the energy contribution of the MO formed between the participating atoms and $E_T(atom-atom, msp^3.AO)$, the change in the energy of the AOs or HOs upon forming the bond. From Eqs. (15.39-15.40), $E_T(MO)$ is

$$E_T(MO) = E(basis\ energies) + E_T(atom-atom, msp^3.AO) \quad (15.43)$$

During bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy $\bar{E}_{osc}$ is the sum of the Doppler, $\bar{E}_D$, and average vibrational kinetic energies, $\bar{E}_{Kvib}$:

$$\overline{E}_{osc} = n_1\left(\overline{E}_D + \overline{E}_{Kvib}\right) = n_1\left(E_{h\nu}\sqrt{\frac{2\overline{E}_K}{m_e c^2}} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \tag{15.44}$$

where n_1 is the number of equivalent bonds of the MO, k is the spring constant of the equivalent harmonic oscillator, and μ is the reduced mass. The angular frequency of the reentrant oscillation in the transition state corresponding to $\overline{E}_D$ is determined by the force between the central field and the electrons in the transition state. The force and its derivative are given by

$$f(R) = -c_{BO}\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3} \tag{15.45}$$

and

$$f'(a) = 2c_{BO}\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3} \tag{15.46}$$

such that the angular frequency of the oscillation in the transition state is given by

$$\omega = \sqrt{\frac{\left[\frac{-3}{a}f(a) - f'(a)\right]}{m_e}} = \sqrt{\frac{k}{m_e}} = \sqrt{\frac{c_{BO}\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}}{m_e}} \tag{15.47}$$

where R is the semimajor axis a or the semiminor axis b depending on the eccentricity of the bond that is most representative of the oscillation in the transition state, c_{BO} is the bond-order factor which is 1 for a single bond and when the MO comprises n_1 equivalent single bonds as in the case of functional groups. c_{BO} is 4 for an independent double bond as in the case of the CO_2 and NO_2 molecules and 9 for an independent triplet bond. C_{1o} is the fraction of the H_2-type ellipsoidal MO basis function of the oscillatory transition state of a chemical bond of the group, and C_{2o} is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the transition state of the chemical bond. Typically, $C_{1o} = C_1$ and $C_{2o} = C_2$. The kinetic energy, E_K, corresponding to $\overline{E}_D$ is given by Planck's equation for functional groups:

$$\overline{E}_K = \hbar\omega = \hbar\sqrt{\frac{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}}{m_e}} \tag{15.48}$$

The Doppler energy of the electrons of the reentrant orbit is

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{m_ec^2}} = E_{h\nu}\sqrt{\frac{2\hbar\sqrt{\frac{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0R^3}}{m_e}}}{m_ec^2}} \tag{15.49}$$

$\overline{E}_{osc}$ given by the sum of $\overline{E}_D$ and $\overline{E}_{Kvib}$ is

$$\overline{E}_{osc}(group) = n_1\left(\overline{E}_D + \overline{E}_{Kvib}\right) = n_1\left(E_{h\nu}\sqrt{\frac{2\hbar\sqrt{\frac{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0R^3}}{m_e}}}{m_ec^2}} + E_{vib} \right) \tag{15.50}$$

$E_{h\nu}$ of a group having n_1 bonds is given by $E_T(MO)/n_1$ such that

$$\overline{E}_{osc} = n_1\left(\overline{E}_D + \overline{E}_{Kvib}\right) = n_1\left(E_T(MO)/n_1\sqrt{\frac{2\overline{E}_K}{Mc^2}} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right) \tag{15.51}$$

$E_{T+osc}(Group)$ is given by the sum of $E_T(MO)$ (Eq. (15.42)) and $\overline{E}_{osc}$ (Eq. (15.51)):

$$\begin{aligned} E_{T+osc}(Group) &= E_T(MO) + \overline{E}_{osc} \\ &= \left(\begin{array}{l} \left(\begin{array}{l} \dfrac{-n_1e^2}{8\pi\varepsilon_0\sqrt{\dfrac{aa_0}{2C_1C_2}}}\left[c_1c_2\left(2-\dfrac{a_0}{a}\right)\ln\dfrac{a+\sqrt{\dfrac{aa_0}{2C_1C_2}}}{a-\sqrt{\dfrac{aa_0}{2C_1C_2}}} - 1 \right] \\ + E_T(AO/HO) + E_T(atom-atom,msp^3.AO) \end{array} \right) \\ \left[1 + \sqrt{\dfrac{2\hbar\sqrt{\dfrac{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_oR^3}}{m_e}}}{m_ec^2}} \right] + n_1\dfrac{1}{2}\hbar\sqrt{\dfrac{k}{\mu}} \end{array} \right) \\ &= \left(E(basis\ energies) + E_T(atom-atom,msp^3.AO)\right)\left[1 + \sqrt{\dfrac{2\hbar\sqrt{\dfrac{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_oR^3}}{m_e}}}{m_ec^2}} \right] + n_1\dfrac{1}{2}\hbar\sqrt{\dfrac{k}{\mu}} \end{aligned} \tag{15.52}$$

The total energy of the functional group $E_T(group)$ is the sum of the total energy of the components comprising the energy contribution of the MO formed between the participating atoms, $E(basis\ energies)$, the change in the energy of the AOs or HOs upon forming the bond ($E_T(atom-atom, msp^3.AO)$), the energy of oscillation in the transition state, and the change in magnetic energy with bond formation, E_{mag}. From Eq. (15.52), the total energy of the group $E_T(Group)$ is

$$E_T(Group) = \left(\begin{array}{l} \left(E(basis\ energies) + E_T\left(atom-atom, msp^3.AO\right)\right)\left[1+\sqrt{\dfrac{2\hbar\sqrt{\dfrac{\dfrac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o R^3}}{m_e}}}{m_ec^2}}\right] \\ +n_1\bar{E}_{Kvib} + E_{mag} \end{array} \right) \quad (15.53)$$

The change in magnetic energy E_{mag} which arises due to the formation of unpaired electrons in the corresponding fragments relative to the bonded group is given by

$$E_{mag} = c_3\frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 r^3} = c_3\frac{8\pi\mu_o\mu_B^2}{r^3} \quad (15.54)$$

where r^3 is the radius of the atom that reacts to form the bond and c_3 is the number of electron pairs.

$$E_T(Group) = \left(\begin{array}{l} \left(E(basis\ energies) + E_T\left(atom-atom, msp^3.AO\right)\right)\left[1+\sqrt{\dfrac{2\hbar\sqrt{\dfrac{\dfrac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o R^3}}{m_e}}}{m_ec^2}}\right] \\ +n_1\bar{E}_{Kvib} + c_3\dfrac{8\pi\mu_o\mu_B^2}{r^3} \end{array} \right) \quad (15.55)$$

The total bond energy of the group $E_D(Group)$ is the negative difference of the total energy of the group (Eq. (15.55)) and the total energy of the starting species given by the sum of $c_4E_{initial}(c_4\ AO/HO)$ and $c_5E_{initial}(c_5\ AO/HO)$:

$$E_D(Group) = -\left(\begin{array}{l} \left(E(basis\ energies) + E_T(atom-atom, msp^3.AO)\right)\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o R^3}}{m_e}}}{m_e c^2}}\right] \\ +n_1\overline{E}_{Kvib} + c_3\frac{8\pi\mu_o\mu_B^2}{r_n^3} - \left(c_4 E_{initial}(AO/HO) + c_5 E_{initial}(c_5\ AO/HO)\right) \end{array} \right) \quad (15.56)$$

In the case of organic molecules, the atoms of the functional groups are energy matched to the $C2sp^3$ HO such that

$$E(AO/HO) = -14.63489\ eV \quad (15.57)$$

For examples of E_{mag} from previous sections:

$$E_{mag}(C2sp^3) = c_3\frac{8\pi\mu_o\mu_B^2}{r^3} = c_3\frac{8\pi\mu_o\mu_B^2}{(0.91771a_0)^3} = c_3 0.14803\ eV \quad (15.58)$$

$$E_{mag}(O2p) = c_3\frac{8\pi\mu_o\mu_B^2}{r^3} = c_3\frac{8\pi\mu_o\mu_B^2}{a_0^3} = c_3 0.11441\ eV \quad (15.59)$$

$$E_{mag}(N2p) = c_3\frac{8\pi\mu_o\mu_B^2}{r^3} = c_3\frac{8\pi\mu_o\mu_B^2}{(0.93084a_0)^3} = c_3 0.14185\ eV \quad (15.60)$$

In the general case of the solution of an organic functional group, the geometric bond parameters are solved from the semimajor axis and the relationships between the parameters by first using Eq. (15.42) to arrive at a. Then, the remaining parameters are determined using Eqs. (15.1-15.5). Next, the energies are given by Eqs. (15.52-15.59). To meet the equipotential condition for the union of the H_2-type-ellipsoidal-MO and the HO or AO of the atom of a functional group, the factor c_2 of a H_2-type ellipsoidal MO in principal Eqs. (15.42) and (15.52) may given by

(i) one:

$$c_2 = 1 \quad (15.61)$$

(ii) the ratio that is less than one of $13.605804\ eV$, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243), and the magnitude of the

Coulombic energy of the participating AO or HO of the atom, $E_{Coulomb}\left(MO.atom, msp^3\right)$ given by Eqs. (15.19) and (15.31-15.32). For $\left|E_{Coulomb}\left(MO.atom, msp^3\right)\right| > 13.605804\ eV$:

$$c_2 = \frac{\dfrac{e^2}{8\pi\varepsilon_0 a_0}}{\dfrac{e^2}{8\pi\varepsilon_0 r_{A-B\ AorBsp^3}}} = \frac{13.605804\ eV}{\left|E_{Coulomb}\left(MO.atom, msp^3\right)\right|} \tag{15.62}$$

For $\left|E_{Coulomb}\left(MO.atom, msp^3\right)\right| < 13.605804\ eV$:

$$c_2 = \frac{\dfrac{e^2}{8\pi\varepsilon_0 r_{A-B\ AorBsp^3}}}{\dfrac{e^2}{8\pi\varepsilon_0 a_0}} = \frac{\left|E_{Coulomb}\left(MO.atom, msp^3\right)\right|}{13.605804\ eV} \tag{15.63}$$

(iii) the ratio that is less than one of $13.605804\ eV$, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243), and the magnitude of the valence energy, $E(valence)$, of the participating AO or HO of the atom where $E(valence)$ is the ionization energy or $E\left(MO.atom, msp^3\right)$ given by Eqs. (15.20) and (15.31-15.32). For $\left|E(valence)\right| > 13.605804\ eV$:

$$c_2 = \frac{\dfrac{e^2}{8\pi\varepsilon_0 a_0}}{\dfrac{e^2}{8\pi\varepsilon_0 r_{A-B\ AorBsp^3}}} = \frac{13.605804\ eV}{\left|E(valence)\right|} \tag{15.64}$$

For $\left|E(valence)\right| < 13.605804\ eV$:

$$c_2 = \frac{\dfrac{e^2}{8\pi\varepsilon_0 r_{A-B\ AorBsp^3}}}{\dfrac{e^2}{8\pi\varepsilon_0 a_0}} = \frac{\left|E(valence)\right|}{13.605804\ eV} \tag{15.65}$$

(iv) the ratio that is less than one of the magnitude of the Coulombic energy of the participating AO or HO of a first atom, $E_{Coulomb}\left(MO.atom, msp^3\right)$ given by Eqs. (15.19) and (15.31-15.32), and the magnitude of the valence energy, $E(valence)$, of the participating AO or HO of a second atom to which the first is energy matched where $E(valence)$ is the

ionization energy or $E\left(MO.atom,msp^3\right)$ given by Eqs. (15.20) and (15.31-15.32). For $\left|E_{Coulomb}\left(MO.atom,msp^3\right)\right| > E(valence)$:

$$c_2 = \frac{|E(valence)|}{\left|E_{Coulomb}\left(MO.atom,msp^3\right)\right|} \tag{15.66}$$

For $\left|E_{Coulomb}\left(MO.atom,msp^3\right)\right| < E(valence)$:

$$c_2 = \frac{\left|E_{Coulomb}\left(MO.atom,msp^3\right)\right|}{|E(valence)|} \tag{15.67}$$

(v) the ratio that is less than one of the magnitude of the valence-level energies, $E_n(valence)$, of the AO or HO of the nth participating atom of two that are energy matched where $E(valence)$ is the ionization energy or $E\left(MO.atom,msp^3\right)$ given by Eqs. (15.20) and (15.31-15.32):

$$c_2 = \frac{E_1(valence)}{E_2(valence)} \tag{15.68}$$

(vi) the factor that is the ratio of the hybridization factor $c_2(1)$ of the valence AO or HO of a first atom and the hybridization factor $c_2(2)$ of the valence AO or HO of a second atom to which the first is energy matched where $c_2(n)$ is given by Eqs. (15.62-15.68); alternatively c_2 is the hybridization factor $c_2(1)$ of the valence AOs or HOs a first pair of atoms and the hybridization factor $c_2(2)$ of the valence AO or HO a third atom or second pair to which the first two are energy matched:

$$c_2 = \frac{c_2(1)}{c_2(2)} \tag{15.69}$$

(vii) the factor that is the product of the hybridization factor $c_2(1)$ of the valence AO or HO of a first atom and the hybridization factor $c_2(2)$ of the valence AO or HO of a second atom to which the first is energy matched where $c_2(n)$ is given by Eqs. (15.62-15.69);

alternatively c_2 is the hybridization factor $c_2(1)$ of the valence AOs or HOs a first pair of atoms and the hybridization factor $c_2(2)$ of the valence AO or HO a third atom or second pair to which the first two are energy matched:

$$c_2 = c_2(1)c_2(2) \tag{15.70}$$

The hybridization factor c_2 corresponds to the force constant k (Eqs. (11.65) and (13.58)). In the case that the valence or Coulombic energy of the AO or HO is less than 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243), then C_2 corresponding to k' (Eq. (15.1)) is given by Eqs. (15.62-15.70).

Specific examples of the factors c_2 and C_2 of a H_2-type ellipsoidal MO of Eq. (15.51) given in following sections are

$$c_2(C2sp^3HO\ to\ F) = \frac{E(C,2sp^3)}{E(F)}c_2(C2sp^3HO) = \frac{-14.63489\ eV}{-17.42282\ eV}(0.91771) = 0.77087;$$

$$C_2(C2sp^3HO\ to\ Cl) = \frac{E(Cl)}{E(C,2sp^3)}c_2(C2sp^3HO) = \frac{-12.96764\ eV}{-14.63489\ eV}(0.91771) = 0.81317;$$

$$C_2(C2sp^3HO\ to\ Br) = \frac{E(Br)}{E(C,2sp^3)}c_2(C2sp^3HO) = \frac{-11.81381\ eV}{-14.63489\ eV}(0.91771) = 0.74081;$$

$$C_2(C2sp^3HO\ to\ I) = \frac{E(I)}{E(C,2sp^3)}c_2(C2sp^3HO) = \frac{-10.45126\ eV}{-14.63489\ eV}(0.91771) = 0.65537;$$

$$c_2(C2sp^3HO\ to\ O) = \frac{E(O)}{E(C,2sp^3)}c_2(C2sp^3HO) = \frac{-13.61806\ eV}{-14.63489\ eV}(0.91771) = 0.85395;$$

$$c_2(H\ to\ 1°N) = \frac{E(N)}{E(C,2sp^3)} = \frac{-14.53414\ eV}{-15.35946\ eV} = 0.94627;$$

$$c_2(C2sp^3HO\ to\ N) = \frac{E(N)}{E(C,2sp^3)}c_2(C2sp^3HO) = \frac{-14.53414\ eV}{-14.63489\ eV}(0.91771) = 0.91140;$$

$$c_2(H\ to\ 2°N) = \frac{E(N)}{E(C,2sp^3)} = \frac{-14.53414\ eV}{-15.56407\ eV} = 0.93383;$$

$$C_2(S3p\ to\ H) = \frac{E(S,3p)}{E(H)} = \frac{-10.36001\ eV}{-13.60580\ eV} = 0.76144;$$

$$C_2(C2sp^3HO\ to\ S) = \frac{E(S)}{E(C,2sp^3)}c_2(C2sp^3HO) = \frac{-10.36001\ eV}{-14.63489\ eV}(0.91771) = 0.64965;$$

$$\begin{aligned} c_2\left(O \text{ to } S3sp^3 \text{ to } C2sp^3HO\right) &= \frac{E(O)}{E(S)} c_2\left(C2sp^3HO\right) \\ &= \frac{-13.61806\ eV}{-10.36001\ eV}(0.91771); \\ &= 1.20632 \end{aligned}$$

$$c_2\left(S3sp^3\right) = \frac{E_{Coulomb}\left(S3sp^3\right)}{E(H)} = \frac{-11.57099\ eV}{-13.60580\ eV} = 0.85045;$$

$$C_2\left(C2sp^3HO \text{ to } S3sp^3\right) = \frac{E\left(S3sp^3\right)}{E\left(C,2sp^3\right)} c_2\left(S3sp^3\right) = \frac{-11.52126\ eV}{-14.63489\ eV}(0.85045) = 0.66951;$$

$$\begin{aligned} C_2\left(S3sp^3 \text{ to } O \text{ to } C2sp^3HO\right) &= \frac{E\left(S,3sp^3\right)}{E(O,2p)} c_2\left(C2sp^3HO\right) \\ &= \frac{-11.52126\ eV}{-13.61806\ eV}(0.91771); \\ &= 0.77641 \end{aligned}$$

$$\begin{aligned} c_2\left(O \text{ to } N2p \text{ to } C2sp^3HO\right) &= \frac{E(O)}{E(N)} c_2\left(C2sp^3HO\right) \\ &= \frac{-13.61806\ eV}{-14.53414\ eV}(0.91771); \\ &= 0.85987 \end{aligned}$$

$$c_2\left(N2p \text{ to } O2p\right) = \frac{c_2\left(C2sp^3HO \text{ to } N\right)}{c_2\left(C2sp^3HO \text{ to } O\right)} = \frac{0.91140}{0.85395} = 1.06727;$$

$$C_2\left(benzeneC2sp^3HO\right) = c_2\left(benzeneC2sp^3HO\right) = \frac{13.605804\ eV}{15.95955\ eV} = 0.85252;$$

$$\begin{aligned} c_2\left(arylC2sp^3HO \text{ to } O\right) &= \frac{E(O)}{E\left(C,2sp^3\right)} c_2\left(arylC2sp^3HO\right) \\ &= \frac{-13.61806\ eV}{-14.63489\ eV}(0.85252) \quad ; \\ &= 0.79329 \end{aligned}$$

$$c_2\left(H \text{ to anline } N\right) = \frac{E(N)}{E\left(C,2sp^3\right)} = \frac{-14.53414\ eV}{-15.76868\ eV} = 0.92171;$$

$$\begin{aligned} c_2\left(arylC2sp^3HO \text{ to } N\right) &= \frac{E(N)}{E\left(C,2sp^3\right)} c_2\left(arylC2sp^3HO\right) \\ &= \frac{-14.53414\ eV}{-14.63489\ eV}(0.85252) \quad , \\ &= 0.84665 \end{aligned}$$

and

$$C_2\left(S3p\ to\ \text{aryl-type}\ C2sp^3HO\right)=\frac{E(S,3p)}{E\left(C,2sp^3\right)}=\frac{-10.36001\ eV}{-15.76868\ eV}=0.65700\ .$$

MO INTERCEPT ANGLES AND DISTANCES

Consider the general case of Eqs. (13.84-13.95) wherein the nucleus of a B atom and the nucleus of a A atom comprise the foci of each H_2-type ellipsoidal MO of an $A-B$ bond. The parameters of the point of intersection of each H_2-type ellipsoidal MO and the A-atom AO are determined from the polar equation of the ellipse:

$$r=r_0\frac{1+e}{1+e\cos\theta'} \tag{15.71}$$

The radius of the A shell is r_A, and the polar radial coordinate of the ellipse and the radius of the A shell are equal at the point of intersection such that

$$r_A=(a-c')\frac{1+\dfrac{c'}{a}}{1+\dfrac{c'}{a}\cos\theta'} \tag{15.72}$$

The polar angle θ' at the intersection point is given by

$$\theta'=\cos^{-1}\left(\frac{a}{c'}\left((a-c')\frac{1+\dfrac{c'}{a}}{a_0}-1\right)\right) \tag{15.73}$$

Then, the angle $\theta_{A\,AO}$ the radial vector of the A AO makes with the internuclear axis is

$$\theta_{A\,AO}=180^\circ-\theta' \tag{15.74}$$

The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals such that the angle $\omega t=\theta_{H_2MO}$ between the internuclear axis and the point of intersection of each H_2-type ellipsoidal MO with the A radial vector obeys the following relationship:

$$r_A\sin\theta_{A\,AO}=b\sin\theta_{H_2MO} \tag{15.75}$$

such that

$$\theta_{H_2MO}=\sin^{-1}\frac{r_a\sin\theta_{A\,AO}}{b} \tag{15.76}$$

The distance d_{H_2MO} along the internuclear axis from the origin of H_2-type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{H_2MO} = a\cos\theta_{H_2MO} \tag{15.77}$$

The distance $d_{A\,AO}$ along the internuclear axis from the origin of the A atom to the point of intersection of the orbitals is given by

$$d_{A\,AO} = c' - d_{H_2MO} \tag{15.78}$$

BOND ANGLES

Further consider an ACB MO comprising a linear combination of $C-A$-bond and $C-B$-bond MOs where C is the general central atom. A bond is also possible between the A and B atoms of the $C-A$ and $C-B$ bonds. Such $A-B$ bonding would decrease the $C-A$ and $C-B$ bond strengths since electron density would be shifted from the latter bonds to the former bond. Thus, the $\angle ACB$ bond angle is determined by the condition that the total energy of the H_2-type ellipsoidal MO between the terminal A and B atoms is zero. The force constant k' of a H_2-type ellipsoidal MO due to the equivalent of two point charges of at the foci is given by:

$$k' = \frac{C_1C_2 2e^2}{4\pi\varepsilon_o} \tag{15.79}$$

where C_1 is the fraction of the H_2-type ellipsoidal MO basis function of a chemical bond of the molecule which is 0.75 (Eq. (13.59)) for a terminal $A-H$ (A is H or other atom) and 1 otherwise and C_2 is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the chemical bond and is equal to the corresponding factor of Eqs. (15.42) and (15.52). The distance from the origin of the MO to each focus c' of the $A-B$ ellipsoidal MO is given by:

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2C_1C_2 a}} = \sqrt{\frac{aa_0}{2C_1C_2}} \tag{15.80}$$

The internuclear distance is

$$2c' = 2\sqrt{\frac{aa_0}{2C_1C_2}} \tag{15.81}$$

The length of the semiminor axis of the prolate spheroidal $A-B$ MO $b=c$ is given by Eq. (15.4).

The component energies and the total energy, $E_T(H_2MO)$, of the $A-B$ bond are given by the energy equations (Eqs. (11.207-11.212), (11.213-11.217), and (11.239)) of H_2 except that the terms based on charge are multiplied by c_{BO}, the bond-order factor which is 1 for a single bond and when the MO comprises n_1 equivalent single bonds as in the case of functional groups. c_{BO} is 4 for an independent double bond as in the case of the CO_2 and NO_2 molecules. The kinetic energy term is multiplied by c'_{BO} which is 1 for a single bond, 2 for a double bond, and 9/2 for a triple bond. The electron energy terms are multiplied by c_1, the fraction of the H_2-type ellipsoidal MO basis function of a terminal chemical bond which is 0.75 (Eq. (13.233)) for a terminal $A-H$ (A is H or other atom) and 1 otherwise. The electron energy terms are further multiplied by c_2', the hybridization or energy-matching factor that results in an equipotential energy match of the participating at least two atomic orbitals of each terminal bond. Furthermore, when $A-B$ comprises atoms other than H, $E_T\left(atom-atom,msp^3.AO\right)$, the energy component due to the AO or HO's charge donation to the terminal MO, is added to the other energy terms to give $E_T(H_2MO)$:

$$E_T(H_2MO)=\frac{-e^2}{8\pi\varepsilon_0 c'}\left[c_1c_2'\left(2c_{BO}-c'_{BO}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]+E_T\left(atom-atom,msp^3.AO\right)$$

(15.82)

The radiation reaction force in the case of the vibration of $A-B$ in the transition state corresponds to the Doppler energy, E_D, given by Eq. (11.181) that is dependent on the motion of the electrons and the nuclei. The total energy that includes the radiation reaction of the $A-B$ MO is given by the sum of $E_T(H_2MO)$ (Eq. (15.82)) and $\overline{E}_{osc}$ given Eqs. (11.213-11.220), (11.231-11.236), and (11.239-11.240). Thus, the total energy $E_T\left(A-B\right)$ of the $A-B$ MO including the Doppler term is

$$E_T(A-B)=\left[\begin{array}{l}\left(\frac{-e^2}{8\pi\varepsilon_0 c'}\left[c_1c_2'\left(2c_{BO}-c'_{BO}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]+E_T(atom-atom,msp^3.AO)\right)\\ \left[1+\sqrt{\frac{2\hbar\sqrt{\frac{c_{BO}\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o a^3}}{m_e}}}{m_ec^2}}\right]+\frac{1}{2}\hbar\sqrt{\frac{c_{BO}\frac{c_1c_2'e^2}{8\pi\varepsilon_o a^3}-\frac{c_{BO}e^2}{8\pi\varepsilon_o(a+c')^3}}{\mu}}\end{array}\right]$$

(15.83)

where C_{1o} is the fraction of the H_2-type ellipsoidal MO basis function of the oscillatory transition state of the $A-B$ bond which is 0.75 (Eq. (13.233)) in the case of H bonding to a central atom and 1 otherwise, C_{2o} is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the transition state of the chemical bond, and $\mu=\frac{m_1m_2}{m_1+m_2}$ is the reduced mass of the nuclei given by Eq. (11.154). To match the boundary condition that the total energy of the $A-B$ ellipsoidal MO is zero, $E_T(A-B)$ given by Eq. (15.83) is set equal to zero. Substitution of Eq. (15.81) into Eq. (15.83) gives

$$0=\left[\begin{array}{l}\left(\frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2C_1C_2}}}\left[c_1c_2'\left(2c_{BO}-c'_{BO}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2C_1C_2}}}{a-\sqrt{\frac{aa_0}{2C_1C_2}}}-1\right]+E_T(atom-atom,msp^3.AO)\right)\\ \left[1+\sqrt{\frac{2\hbar\sqrt{\frac{c_{BO}\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o a^3}}{m_e}}}{m_ec^2}}\right]+\frac{1}{2}\hbar\sqrt{\frac{c_{BO}\frac{c_1c_2'e^2}{8\pi\varepsilon_o a^3}-\frac{c_{BO}e^2}{8\pi\varepsilon_o\left(a+\sqrt{\frac{aa_0}{2C_1C_2}}\right)^3}}{\mu}}\end{array}\right]$$

(15.84)

The vibrational energy-term of Eq. (15.84) is determined by the forces between the central field and the electrons and those between the nuclei (Eqs. (11.141-11.145)). The electron-central-field force and its derivative are given by

$$f(a)=-c_{BO}\frac{c_1c_2'e^2}{4\pi\varepsilon_0 a^3} \qquad (15.85)$$

and

$$f'(a) = 2c_{BO}\frac{c_1c_2'e^2}{4\pi\varepsilon_0 a^3} \tag{15.86}$$

The nuclear repulsion force and its derivative are given by

$$f(a+c') = \frac{e^2}{8\pi\varepsilon_o (a+c')^2} \tag{15.87}$$

and

$$f'(a+c') = -\frac{e^2}{4\pi\varepsilon_o (a+c')^3} \tag{15.88}$$

such that the angular frequency of the oscillation is given by

$$\omega = \sqrt{\frac{\left[\frac{-3}{a}f(a) - f'(a)\right]}{\mu}} = \sqrt{\frac{k}{m_e}} = \sqrt{\frac{c_{BO}\frac{c_1c_2'e^2}{4\pi\varepsilon_0 a^3} - \frac{e^2}{8\pi\varepsilon_0 (a+c')^2}}{\mu}} \tag{15.89}$$

Since both terms of $\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib}$ are small due to the large values of a and c', to very good approximation, a convenient form of Eq. (15.84) which is evaluated to determine the bond angles of functional groups is given by

$$0 = \left[\begin{array}{l} \left(\frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2C_1C_2}}}\left[c_1c_2'\left(2-\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2C_1C_2}}}{a-\sqrt{\frac{aa_0}{2C_1C_2}}} - 1\right] + E_T(atom-atom, msp^3.AO)\right) \\ \left[1+\sqrt{\frac{2\hbar\sqrt{\frac{\frac{c_1e^2}{4\pi\varepsilon_o a^3}}{m_e}}}{m_ec^2}}\right] + \frac{1}{2}\hbar\sqrt{\frac{\frac{c_1e^2}{8\pi\varepsilon_o a^3} - \frac{e^2}{8\pi\varepsilon_o\left(a+\sqrt{\frac{aa_0}{2C_1C_2}}\right)^3}}{\mu}} \end{array}\right] \tag{15.90}$$

From the energy relationship given by Eq. (15.90) and the relationship between the axes given by Eqs. (15.2-15.5), the dimensions of the $A-B$ MO can be solved. The most convenient way to solve Eq. (15.90) is by the reiterative technique using a computer.

A factor c_2 of a given atom in the determination of c_2' for calculating the zero of the total $A-B$ bond energy is typically given by Eqs. (15.62-15.65). In the case of a $H-H$ terminal bond of an alkyl or alkenyl group, c_2' is typically the ratio of c_2 of Eq. (15.62) for the $H-H$ bond which is one and c_2 of the carbon of the corresponding $C-H$ bond:

$$c_2' = \frac{1}{c_2(C2sp^3)} = \frac{13.605804\ eV}{E_{Coulomb}\left(C-H\ C2sp^3\right)} \tag{15.91}$$

In the case of the determination of the bond angle of the ACH MO comprising a linear combination of $C-A$-bond and $C-H$-bond MOs where A and C are general, C is the central atom, and c_2 for an atom is given by Eqs. (15.62-15.70), c_2' of the $A-H$ terminal bond is typically the ratio of c_2 of the A atom for the $A-H$ terminal bond and c_2 of the C atom of the corresponding $C-H$ bond:

$$c_2' = \frac{c_2(A(A-H)msp^3)}{c_2(C(C-H)(msp^3)} \tag{15.92}$$

In the case of the determination of the bond angle of the COH MO of an alcohol comprising a linear combination of $C-O$-bond and $O-H$-bond MOs where C, O, and H are carbon, oxygen, and hydrogen, respectively, c_2' of the $C-H$ terminal bond is typically 0.91771 since the oxygen and hydrogen atoms are at the Coulomb potential of a proton and an electron (Eqs. (1.236) and (10.162), respectively) that is energy matched to the $C2sp^3$ HO.

In the determination of the hybridization factor c_2' of Eq. (15.90) from Eqs. (15.62-15.70), the Coulombic energy, $E_{Coulomb}\left(MO.atom, msp^3\right)$, or the energy, $E\left(MO.atom, msp^3\right)$, the radius $r_{A-B\ AorBsp^3}$ of the A or B AO or HO of the heteroatom of the $A-B$ terminal bond MO such as the $C2sp^3$ HO of a terminal $C-C$ bond is calculated using Eq. (15.32) by considering $\sum E_{T_{mol}}\left(MO, 2sp^3\right)$, the total energy donation to each bond with which it participates in bonding as it forms the terminal bond. The Coulombic energy $E_{Coulomb}\left(MO.atom, msp^3\right)$ of the outer electron of the $atom\ msp^3$ shell is given by Eq. (15.19). In the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy $E(magnetic)$ (Eq. (15.15)) at the initial radius r of the AO electron. Then, the energy $E\left(MO.atom, msp^3\right)$ of the outer electron of the $atom\ msp^3$ shell is given by the sum of $E_{Coulomb}\left(MO.atom, msp^3\right)$ and $E(magnetic)$ (Eq. (15.20)).

In the specific case of the terminal bonding of two carbon atoms, the c_2 factor of each carbon given by Eq. (15.62) is determined using the Coulombic energy $E_{Coulomb}\left(C-C\ C2sp^3\right)$ of the outer electron of the $C2sp^3$ shell given by Eq. (15.19) with the

radius $r_{C-C\ C2sp^3}$ of each $C2sp^3$ HO of the terminal $C-C$ bond calculated using Eq. (15.32) by considering $\sum E_{T_{mol}}(MO,2sp^3)$, the total energy donation to each bond with which it participates in bonding as it forms the terminal bond including the contribution of the methylene energy, 0.92918 eV (Eq. (14.513)), corresponding to the terminal $C-C$ bond. The corresponding $E_T(atom-atom,msp^3.AO)$ in Eq. (15.90) is $E_T(C-C\ C2sp^3)=-1.85836\ eV$.

In the case that the terminal atoms are carbon or other heteroatoms, the terminal bond comprises a linear combination of the HOs or AOs; thus, c_2' is the average of the hybridization factors of the participating atoms corresponding to the normalized linear sum:

$$c_2' = \frac{1}{2}\left(c_2'(atom\ 1)+c_2'(atom\ 2)\right) \tag{15.93}$$

In the exemplary cases of $C-C$, $O-O$, and $N-N$ where C is carbon:

$$\begin{aligned} c_2' &= \frac{1}{2}\left(\frac{\dfrac{e^2}{8\pi\varepsilon_0 a_0}}{\dfrac{e^2}{8\pi\varepsilon_0 r_{A-A\ A_1AO/HO}}} + \frac{\dfrac{e^2}{8\pi\varepsilon_0 a_0}}{\dfrac{e^2}{8\pi\varepsilon_0 r_{A-A\ A_2AO/HO}}} \right) \\ &= \frac{1}{2}\left(\frac{13.605804\ eV}{E_{Coulomb}(A-A.A_1AO/HO)} + \frac{13.605804\ eV}{E_{Coulomb}(A-A.A_2AO/HO)} \right) \end{aligned} \tag{15.94}$$

In the exemplary cases of $C-N$, $C-O$, and $C-S$,

$$c_2' = \frac{1}{2}\left(\frac{13.605804\ eV}{E_{Coulomb}(C-B\ C2sp^3)} + c_2(C\ to\ B) \right) \tag{15.95}$$

where C is carbon and $c_2(C\ to\ B)$ is the hybridization factor of Eqs. (15.52) and (15.84) that matches the energy of the atom B to that of the atom C in the group. For these cases, the corresponding $E_T(atom-atom,msp^3.AO)$ term in Eq. (15.90) depends on the hybridization and bond order of the terminal atoms in the molecule, but typical values matching those used in the determination of the bond energies (Eq. (15.56)) are

$E_T(C-O\ C2sp^3.O2p)=-1.44915\ eV$; $E_T(C-O\ C2sp^3.O2p)=-1.65376\ eV$;

$E_T(C-N\ C2sp^3.N2p)=-1.44915\ eV$; $E_T(C-S\ C2sp^3.S2p)=-0.72457\ eV$;

$E_T(O-O\ O2p.O2p)=-1.44915\ eV$; $E_T(O-O\ O2p.O2p)=-1.65376\ eV$;

$E_T\left(N-N\ N2p.N2p\right)=-1.44915\ eV$; $E_T\left(N-O\ N2p.O2p\right)=-1.44915\ eV$; $E_T\left(F-F\ F2p.F2p\right)=-1.44915\ eV$; $E_T\left(Cl-Cl\ Cl3p.Cl3p\right)=-0.92918\ eV$; $E_T\left(Br-Br\ Br4p.Br4p\right)=-0.92918\ eV$; $E_T\left(I-I\ I5p.I5p\right)=-0.36229\ eV$; $E_T\left(C-F\ C2sp^3.F2p\right)=-1.85836\ eV$; $E_T\left(C-Cl\ C2sp^3.Cl3p\right)=-0.92918\ eV$; $E_T\left(C-Br\ C2sp^3.Br4p\right)=-0.72457\ eV$; $E_T\left(C-I\ C2sp^3.I5p\right)=-0.36228\ eV$, and $E_T\left(O-Cl\ O2p.Cl3p\right)=-0.92918\ eV$.

In the case that the terminal bond is $X-X$ where X is a halogen atom, c_1 is one, and c_2' is the average (Eq. (15.93)) of the hybridization factors of the participating halogen atoms given by Eqs. (15.62-15.63) where $E_{Coulomb}\left(MO.atom, msp^3\right)$ is determined using Eq. (15.32) and $E_{Coulomb}\left(MO.atom, msp^3\right)=13.605804\ eV$ for $X=I$. The factor C_1 of Eq. (15.90) is one for all halogen atoms. The factor C_2 of fluorine is one since it is the only halogen wherein the ionization energy is greater than that $13.605804\ eV$, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). For each of the other halogens, Cl, Br, and I, C_2 is the hybridization factor of Eq. (15.52) given by Eq. (15.70) with $c_2(1)$ being that of the halogen given by Eq. (15.68) that matches the valence energy of X ($E_1(valence)$) to that of the $C2sp^3$ HO ($E_2(valence)=-14.63489\ eV$, Eq. (15.25)) and to the hybridization of $C2sp^3$ HO ($c_2(2)=0.91771$, Eq. (13.430)). $E_T\left(atom-atom, msp^3.AO\right)$ of Eq. (15.90) is the maximum for the participating atoms which is $-1.44915\ eV$, $-0.92918\ eV$, $-0.92918\ eV$, and $-0.33582\ eV$ for F, Cl, Br, and I, respectively.

Consider the case that the terminal bond is $C-X$ where C is a carbon atom and X is a halogen atom. The factors c_1 and C_1 of Eq. (15.90) are one for all halogen atoms. For $X=F$, c_2' is the average (Eq. (15.95)) of the hybridization factors of the participating carbon and F atoms where c_2 for carbon is given by Eq. (15.62) and c_2 for fluorine matched to carbon is given by Eq. (15.70) with $c_2(1)$ for the fluorine atom given by Eq. (15.68) that matches the valence energy of F ($E_1(valence)=-17.42282\ eV$) to that of the $C2sp^3$ HO

($E_2(valence) = -14.63489\ eV$, Eq. (15.25)) and to the hybridization of $C2sp^3$ HO ($c_2(2) = 0.91771$, Eq. (13.430)). The factor C_2 of fluorine is one since it is the only halogen wherein the ionization energy is greater than that $13.605804\ eV$, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). For each of the other halogens, Cl, Br, and I, c_2' is the hybridization factor of the participating carbon atom since the halogen atom is energy matched to the carbon atom. C_2 of the terminal-atom bond matches that used to determine the energies of the corresponding $C-X$-bond MO. Then, C_2 is the hybridization factor of Eq. (15.52) given by Eq. (15.70) with $c_2(1)$ for the halogen atom given by Eq. (15.68) that matches the valence energy of X ($E_1(valence)$) to that of the $C2sp^3$ HO ($E_2(valence) = -14.63489\ eV$, Eq. (15.25)) and to the hybridization of $C2sp^3$ HO ($c_2(2) = 0.91771$, Eq. (13.430)). $E_T(atom-atom, msp^3.AO)$ of Eq. (15.90) is the maximum for the participating atoms which is $-1.85836\ eV$, $-0.92918\ eV$, $-0.72457\ eV$, and $-0.33582\ eV$ for F, Cl, Br, and I, respectively.

Consider the case that the terminal bond is $H-X$ corresponding to the angle of the atoms HCX where C is a carbon atom and X is a halogen atom. The factors c_1 and C_1 of Eq. (15.90) are 0.75 for all halogen atoms. For $X = F$, c_2' is given by Eq. (15.69) with c_2 of the participating carbon and F atoms given by Eq. (15.62) and Eq. (15.65), respectively. The factor C_2 of fluorine is one since it is the only halogen wherein the ionization energy is greater than that $13.605804\ eV$, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). For each of the other halogens, Cl, Br, and I, c_2' is also given by Eq. (15.69) with c_2 of the participating carbon given by Eq. (15.62) and c_2 of the participating X atom given by $c_2 = 0.91771$ (Eq. (13.430)) since the X atom is energy matched to the $C2sp^3$ HO. In these cases, C_2 is given by Eq. (15.65) for the corresponding atom X where C_2 matches the energy of the atom X to that of H.

Using the distance between the two atoms A and B of the general molecular group ACB when the total energy of the corresponding $A-B$ MO is zero, the corresponding bond angle can be determined from the law of cosines:

$$s_1^2 + s_2^2 - 2s_1s_2\text{cosine}\theta = s_3^2 \tag{15.96}$$

With $s_1 = 2c'_{C-A}$, the internuclear distance of the $C-A$ bond, $s_2 = 2c'_{C-B}$, the internuclear distance of each $C-B$ bond, and $s_3 = 2c'_{A-B}$, the internuclear distance of the two terminal atoms, the bond angle $\theta_{\angle ACB}$ between the $C-A$ and $C-B$ bonds is given by

$$\left(2c'_{C-A}\right)^2 + \left(2c'_{C-B}\right)^2 - 2\left(2c'_{C-A}\right)\left(2c'_{C-B}\right)\text{cosine}\,\theta = \left(2c'_{A-B}\right)^2 \tag{15.97}$$

$$\theta_{\angle ACB} = \cos^{-1}\left(\frac{\left(2c'_{C-A}\right)^2 + \left(2c'_{C-B}\right)^2 - \left(2c'_{A-B}\right)^2}{2\left(2c'_{C-A}\right)\left(2c'_{C-B}\right)}\right) \tag{15.98}$$

Consider the exemplary structure $C_bC_a(O_a)O_b$ wherein C_a is bound to C_b, O_a, and O_b. In the general case that the three bonds are coplanar and two of the angles are known, say θ_1 and θ_2, then the third θ_3 can be determined geometrically:

$$\theta_3 = 360 - \theta_1 - \theta_2 \tag{15.99}$$

In the general case that two of the three coplanar bonds are equivalent and one of the angles is known, say θ_1, then the second and third can be determined geometrically:

$$\theta_2 = \theta_3 = \frac{\left(360 - \theta_1\right)}{2} \tag{15.100}$$

ANGLES AND DISTANCES FOR AN MO THAT FORMS AN ISOSCELES TRIANGLE

In the general case where the group comprises three $A-B$ bonds having B as the central atom at the apex of a pyramidal structure formed by the three bonds with the A atoms at the base in the xy-plane. The C_{3v} axis centered on B is defined as the vertical or z-axis, and any two $A-B$ bonds form an isosceles triangle. Then, the angle of the bonds and the distances from and along the z-axis are determined from the geometrical relationships given by Eqs. (13.412-13.416):

the distance $d_{origin-B}$ from the origin to the nucleus of a terminal B atom is given by

$$d_{origin-B} = \frac{2c'_{B-B}}{2\sin 60°} \tag{15.101}$$

the height along the z-axis from the origin to the A nucleus d_{height} is given by

$$d_{height} = \sqrt{\left(2c'_{A-B}\right)^2 - \left(d_{origin-B}\right)^2}\text{, and} \tag{15.102}$$

the angle θ_v of each $A-B$ bond from the z-axis is given by

$$\theta_v = \tan^{-1}\left(\frac{d_{origin-B}}{d_{height}}\right) \tag{15.103}$$

Consider the case where the central atom B is further bound to a fourth atom C and the $B-C$ bond is along the z-axis. Then, the bond $\theta_{\angle ABC}$ given by Eq. (14.206) is

$$\theta_{\angle ABC} = 180 - \theta_v \tag{15.104}$$

DIHEDRAL ANGLE

Consider the plane defined by a general ACA MO comprising a linear combination of two $C-A$-bond MOs where C is the central atom. The dihedral angle $\theta_{\angle BC/ACA}$ between the ACA-plane and a line defined by a third bond with C, specifically that corresponding to a $C-B$-bond MO, is calculated from the bond angle $\theta_{\angle ACA}$ and the distances between the A, B, and C atoms. The distance d_1 along the bisector of $\theta_{\angle ACA}$ from C to the internuclear-distance line between A and A, $2c'_{A-A}$, is given by

$$d_1 = 2c'_{C-A}\cos\frac{\theta_{\angle ACA}}{2} \tag{15.105}$$

where $2c'_{C-A}$ is the internuclear distance between A and C. The atoms A, A, and B define the base of a pyramid. Then, the pyramidal angle $\theta_{\angle ABA}$ can be solved from the internuclear distances between A and A, $2c'_{A-A}$, and between A and B, $2c'_{A-B}$, using the law of cosines (Eq. (15.98)):

$$\theta_{\angle ABA} = \cos^{-1}\left(\frac{(2c'_{A-B})^2 + (2c'_{A-B})^2 - (2c'_{A-A})^2}{2(2c'_{A-B})(2c'_{A-B})}\right) \tag{15.106}$$

Then, the distance d_2 along the bisector of $\theta_{\angle ABA}$ from B to the internuclear-distance line $2c'_{A-A}$, is given by

$$d_2 = 2c'_{A-B}\cos\frac{\theta_{\angle ABA}}{2} \tag{15.107}$$

The lengths d_1, d_2, and $2c'_{C-B}$ define a triangle wherein the angle between d_1 and the internuclear distance between B and C, $2c'_{C-B}$, is the dihedral angle $\theta_{\angle BC/ACA}$ that can be solved using the law of cosines (Eq. (15.98)):

$$\theta_{\angle BC/ACA} = \cos^{-1}\left(\frac{d_1^2 + \left(2c'_{C-B}\right)^2 - d_2^2}{2d_1\left(2c'_{B-C}\right)}\right) \tag{15.108}$$

SOLUTION OF GEOMETRICAL AND ENERGY PARAMETERS OF MAJOR FUNCTIONAL GROUPS AND CORRESPONDING ORGANIC MOLECULES

The exemplary molecules given in the following sections were solved using the solutions of organic chemical functional groups as basis elements wherein the structures and energies where linearly added to achieve the molecular solutions. Each functional group can be treated as a building block to form any desired molecular solution from the corresponding linear combination. Each functional group element was solved using the atomic orbital and hybrid orbital spherical orbitsphere solutions bridged by molecular orbitals comprised of the H_2-type prolate spheroidal solution given in the Nature of the Chemical Bond of Hydrogen-Type Molecules section. The energy of each MO was matched at the HO or AO by matching the hybridization and total energy of the MO to the AOs and HOs. The energy E_{mag} (e.g. given by Eq. (15.58)) for a $C2sp^3$ HO and Eq.(15.59) for an $O2p$ AO) was subtracted for each set of unpaired electrons created by bond breakage.

The bond energy is not equal to the component energy of each bond as it exists in the molecule; although, they are close. The total energy of each group is its contribution to the total energy of the molecule as a whole. The determination of the bond energies for the creation of the separate parts must take into account the energy of the formation of any radicals and any redistribution of charge density within the pieces and the corresponding energy change with bond cleavage. Also, the vibrational energy in the transition state is dependent on the other groups that are bound to a given functional group. This will effect the functional-group energy. But, because the variations in the energy based on the balance of the molecular composition are typically of the order of a few hundreds of electron volts at most, they were neglected.

The energy of each functional-group MO bonding to a given carbon HO is independently matched to the HO by subtracting the contribution to the change in the energy of the HO from the total MO energy given by the sum of the MO contributions and $E\left(C,2sp^3\right) = -14.63489\ eV$ (Eq. (13.428)). The intercept angles are determined from Eqs.

(15.71-15.78) using the final radius of the HO of each atom. The final carbon-atom radius is determined using Eqs. (15.32) wherein the sum of the energy contributions of each atom to all the MOs in which it participates in bonding is determined. This final radius is used in Eqs. (15.19) and (15.20) to calculate the final valence energy of the HO of each atom at the corresponding final radius. The radius of any bonding heteroatom that contributes to a MO is calculated in the same manner, and the energy of its outermost shell is matched to that of the MO by the hybridization factor between the carbon-HO energy and the energy of the heteroatomic shell. The donation of electron density to the AOs and HOs reduces the energy. The donation of the electron density to the MO's at each AO or HO is that which causes the resulting energy to be divided equally between the participating AOs or HOs to achieve energy matching.

The molecular solutions can be used to design synthetic pathways and predict product yields based on equilibrium constants calculated from the heats of formation. New stable compositions of matter can be predicted as well as the structures of combinatorial chemistry reactions. Further important pharmaceutical applications include the ability to graphically or computationally render the structures of drugs that permit the identification of the biologically active parts of the molecules to be identified from the common spatial charge-density functions of a series of active molecules. Drugs can be designed according to geometrical parameters and bonding interactions with the data of the structure of the active site of the drug.

To calculate conformations, folding, and physical properties, the exact solutions of the charge distributions in any given molecule are used to calculate the fields, and from the fields, the interactions between groups of the same molecule or between groups on different molecules are calculated wherein the interactions are distance and relative orientation dependent. The fields and interactions can be determined using a finite-element-analysis approach of Maxwell's equations.

AROMATIC AND HETEROCYCLIC COMPOUNDS

Aromatic and heterocyclic molecules comprise at least one of an aromatic or a cyclic conjugated alkene functional group. The latter was described in the Cyclic and Conjugated Alkenes section. The aromatic bond is uniquely stable and requires the sharing of the electrons of multiple H_2-type MOs. The results of the derivation of the parameters of the benzene molecule given in the Benzene Molecule (C_6H_6) section can be generalized to any aromatic function group(s) of aromatic and heterocyclic compounds.

C_6H_6 can be considered a linear combination of three ethylene molecules wherein a $C-H$ bond of each CH_2 group of $H_2C=CH_2$ is replaced by a $C=C$ bond to form a six-member ring of carbon atoms. The solution of the ethylene molecule is given in the Ethylene Molecule (CH_2CH_2) section. The radius $r_{ethylene2sp^3}$ ($0.85252a_0$) of the $C2sp^3$ shell of ethylene calculated from the Coulombic energy is given by Eq. (14.244). The Coulombic energy $E_{Coulomb}\left(C_{ethylene},2sp^3\right)$ ($-15.95955\ eV$) of the outer electron of the $C2sp^3$ shell is given by Eq. (14.245). The energy $E\left(C_{ethylene},2sp^3\right)$ ($-15.76868\ eV$) of the outer electron of the $C2sp^3$ shell is given by Eq. (14.246). $E_T\left(C=C,2sp^3\right)$ ($-1.13380\ eV$) (Eq. (14.247), the energy change of each $C2sp^3$ shell with the formation of the $C=C$-bond MO is given by the difference between $E\left(C_{ethylene},2sp^3\right)$ and $E\left(C,2sp^3\right)$. C_6H_6 can be solved using the same principles as those used to solve ethylene wherein the $2s$ and $2p$ shells of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. Each $2sp^3$ HO of each carbon atom initially has four unpaired electrons. Thus, the $6\,H$ atomic orbitals (AOs) of benzene contribute six electrons and the six sp^3-hybridized carbon atoms contribute twenty-four electrons to form six $C-H$ bonds and six $C=C$ bonds. Each $C-H$ bond has two paired electrons with one donated from the H AO and the other from the $C2sp^3$ HO. Each $C=C$ bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from two sets of two $C2sp^3$ HOs of the participating carbon atoms. Each $C-H$ and each $C=C$ bond comprises a linear combination of one and two diatomic H_2-type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section, respectively.

Consider the case where three sets of $C=C$-bond MOs form bonds between the two carbon atoms of each molecule to form a six-member ring such that the six resulting bonds comprise eighteen paired electrons. Each bond comprises a linear combination of two MOs wherein each comprises two $C2sp^3$ HOs and 75% of a H_2-type ellipsoidal MO divided between the $C2sp^3$ HOs:

$$\begin{pmatrix} 3\left(2\ C2sp^3+0.75\ H_2\ MO\right)\rightarrow 3\left(C\overset{4e}{=}C\right)-ethylene-type-bond\ MO \\ \rightarrow 6\left(C\overset{3e}{=}C\right)-bond\ MO\ of\ benzene \end{pmatrix} \tag{15.142}$$

The linear combination of each H_2-type ellipsoidal MO with each $C2sp^3$ HO further comprises an excess 25% charge-density contribution per bond from each $C2sp^3$ HO to the $C=C$-bond MO to achieve an energy minimum. Thus, the dimensional parameters of each bond $C=C$-bond are determined using Eqs. (15.42) and (15.1-15.5) in a form that are the same equations as those used to determine the same parameters of the $C=C$-bond MO of ethylene (Eqs. (14.242-14.268)) while matching the boundary conditions of the structure of benzene.

Hybridization with 25% electron donation to each $C=C$-bond gives rise to the $C_{benzene}2sp^3$ HO-shell Coulombic energy $E_{Coulomb}\left(C_{benzene},2sp^3\right)$ given by Eq. (14.245). To meet the equipotential condition of the union of the six $C2sp^3$ HOs, c_2 and C_2 of Eq. (15.42) for the aromatic $C\overset{3e}{=}C$-bond MO is given by Eq. (15.62) as the ratio of 15.95955 eV, the magnitude of $E_{Coulomb}\left(C_{benzene},2sp^3\right)$ (Eq. (14.245)), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H (Eq. (1.243)):

$$C_2\left(benzeneC2sp^3HO\right)=c_2\left(benzeneC2sp^3HO\right)=\frac{13.605804\ eV}{15.95955\ eV}=0.85252 \qquad (15.143)$$

The energies of each $C\overset{3e}{=}C$ bond of benzene are also determined using the same equations as those of ethylene (Eqs. (14.251-14.253) and (14.319-14.333) with the parameters of benzene. Ethylene serves as a basis element for the $C\overset{3e}{=}C$ bonding of benzene wherein each of the six $C\overset{3e}{=}C$ bonds of benzene comprises $(0.75)(4)=3$ electrons according to Eq. (15.142). The total energy of the bonds of the eighteen electrons of the $C\overset{3e}{=}C$ bonds of benzene, $E_T\left(C_6H_6,C\overset{3e}{=}C\right)$, is given by $(6)(0.75)$ times $E_{T+osc}(C=C)$ (Eq. (14.492)), the total energy of the $C\overset{3e}{=}C$-bond MO of benzene including the Doppler term, minus eighteen times $E\left(C,2sp^3\right)$ (Eq. (14.146)), the initial energy of each $C2sp^3$ HO of each C that forms the $C\overset{3e}{=}C$ bonds of bond order two. Thus, the total energy of the six $C\overset{3e}{=}C$ bonds of benzene with three electron per aromatic bond given by Eq. (14.493) is

$$\begin{aligned}E_T\left(C_6H_6,C\overset{3e}{=}C\right)&=(6)(0.75)E_{T+osc}(C=C)-(6)(3)E\left(C,2sp^3\right)\\&=(6)(0.75)(-66.05796\ eV)-18(-14.63489\ eV)\\&=-297.26081\ eV-(-263.42798\ eV)\\&=-33.83284\ eV\end{aligned} \qquad (15.144)$$

The results of benzene can be generalized to the class of aromatic and heterocyclic compounds. $E_{h\nu}$ of an aromatic bond is given by $E_T(H_2)$ (Eqs. (11.212) and (14.486)), the maximum total energy of each H_2-type MO such that

$$\bar{E}_{osc}=n_1\left(\bar{E}_D+\bar{E}_{Kvib}\right)=n_1\left(-31.63536831\ eV\sqrt{\frac{2\bar{E}_K}{Mc^2}}+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \qquad (15.145)$$

The factor of 0.75 corresponding to the three electrons per aromatic bond of bond order two given in the Benzene Molecule (C_6H_6) section modifies Eqs. (15.52-15.56). Multiplication of

the total energy given by Eq. (15.55) by $f_1 = 0.75$ with the substitution of Eq. (15.145) gives the total energy of the aromatic bond:

$$E_T(Group) = f_1 \left(\begin{array}{l} E(basis\ energies) + E_T(atom-atom, msp^3.AO) \\ -31.63536831\ eV \sqrt{\frac{2\hbar\sqrt{\frac{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o R^3}}{m_e}}}{m_e c^2}} + n_1\bar{E}_{Kvib} + c_3\frac{8\pi\mu_o\mu_B^2}{r^3} \end{array} \right) \quad (15.146)$$

The total bond energy of the aromatic group $E_D(Group)$ is the negative difference of the total energy of the group (Eq. (15.146)) and the total energy of the starting species given by the sum of $c_4E_{initial}(c_4\ AO/HO)$ and $c_5E_{initial}(c_5\ AO/HO)$:

$$E_D(Group) = -\left(\begin{array}{l} f_1 \left(\begin{array}{l} E(basis\ energies) + E_T(atom-atom, msp^3.AO) \\ -31.63536831\ eV \sqrt{\frac{2\hbar\sqrt{\frac{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o R^3}}{m_e}}}{m_e c^2}} + n_1\bar{E}_{Kvib} + c_3\frac{8\pi\mu_o\mu_B^2}{r^3} \end{array} \right) \\ -\left(c_4E_{initial}(AO/HO) + c_5E_{initial}(c_5\ AO/HO)\right) \end{array} \right) \quad (15.147)$$

Since there are three electrons per aromatic bond, c_4 is three times the number of aromatic bonds.

Benzene can also be considered as comprising chemical bonds between six CH radicals wherein each radical comprises a chemical bond between carbon and hydrogen atoms. The solution of the parameters of CH is given in the Hydrogen Carbide (CH) section. Those of the benzene are given in the Benzene Molecule (C_6H_6) section. The energy components of V_e, V_p, T, V_m, and E_T are the same as those of the hydrogen carbide radical, except that $E_T(C=C,2sp^3) = -1.13379\ eV$ (Eq. (14.247)) is subtracted from $E_T(CH)$ of Eq. (13.495) to match the energy of each $C-H$-bond MO to the decrease in the energy of the corresponding $C2sp^3$ HO. In the corresponding generalization of the aromatic CH group, the geometrical parameters are determined using Eq. (15.42) and Eqs. (15.1-15.5) with $E_T(atom-atom, msp^3.AO) = -1.13379\ eV$.

The total energy of the benzene $C-H$-bond MO, $E_{T_{benzene}}(C-H)$, given by Eq. (14.467) is the sum of $0.5E_T(C=C,2sp^3)$, the energy change of each $C2sp^3$ shell per single bond due to the decrease in radius with the formation of the corresponding $C\overset{3e}{=}C$-bond MO (Eq. (14.247)), and $E_{T_{benzene}}(CH)$, the σ MO contribution given by Eq. (14.441). In the corresponding generalization of the aromatic CH group, the energy parameters are determined using Eqs. (15.146-15.147) with $f_1 = 1$ and $E_T(atom-atom, msp^3.AO) = \frac{-1.13379\ eV}{2}$. Thus, the energy

contribution to the single aromatic CH bond is one half that of the $C\overset{3e}{=}C$ double bond contribution. This matches the energies of the CH and $C\overset{3e}{=}C$ aromatic groups, conserves the electron number with the equivalent charge density as that of $s=1$ in Eqs. (15.18-15.21), and further gives a minimum energy for the molecule. Breakage of the aromatic $C\overset{3e}{=}C$ bonds to give CH groups creates unpaired electrons in these fragments that corresponds to $c_3=1$ in Eq. (15.56) with E_{mag} given by Eq. (15.58).

Each of the $C-H$ bonds of benzene comprises two electrons according to Eq. (14.439). From the energy of each $C-H$ bond, $-E_{D_{benzene}}\left({}^{12}CH\right)$ (Eq. (14.477)), the total energy of the twelve electrons of the six $C-H$ bonds of benzene, $E_T\left(C_6H_6,C-H\right)$, given by Eq. (14.494) is

$$E_T\left(C_6H_6,C-H\right)=(6)\left(-E_{D_{benzene}}\left({}^{12}CH\right)\right)=6\left(-3.90454\ eV\right)=-23.42724\ eV \qquad (15.148)$$

The total bond dissociation energy of benzene, $E_D\left(C_6H_6\right)$, given by Eq. (14.495) is the negative sum of $E_T\left(C_6H_6,C\overset{3e}{=}C\right)$ (Eq. (14.493)) and $E_T\left(C_6H_6,C-H\right)$ (Eq. (14.494)):

$$\begin{aligned} E_D\left(C_6H_6\right) &= -\left(E_T\left(C_6H_6,C\overset{3e}{=}C\right)+E_T\left(C_6H_6,C-H\right)\right) \\ &= -\left(\left(-33.83284\ eV\right)+\left(-23.42724\ eV\right)\right) \qquad (15.149) \\ &= 57.2601\ eV \end{aligned}$$

Using the parameters given in Tables 15.214 and 15.216 in the general equations (Eqs. (15.42), (15.1-15.5), and (15.146-15.147)) reproduces the results for benzene given in the Benzene Molecule (C_6H_6) section as shown in Tables 15.214 and 15.216.

The symbols of the functional groups of aromatics and hertocyclics are given in Table 15.213. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of aromatics and hertocyclics are given in Tables 15.214, 15.215, and 15.216, respectively. The total energy of benzene given in Table 15.217 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.216 corresponding to functional-group composition of the molecule. The bond angle parameters of benzene determined using Eqs. (15.79-15.108) are given in Table 15.218.

Table 15.213. The symbols of functional groups of aromatics and hertocyclics.

Functional Group	Group Symbol
CC (aromatic bond)	$C\overset{3e}{=}C$
CH (aromatic)	CH (i)

Table 15.214. The geometrical bond parameters of aromatics and hertocyclics and experimental values [1].

Parameter	$\overset{3e}{C=C}$ Group	CH Group
$a\ (a_0)$	1.47348	1.60061
$c'\ (a_0)$	1.31468	1.03299
Bond Length $2c'$ (□)	1.39140	1.09327
Exp. Bond Length (□)	1.399 (benzene)	1.101 (benzene)
$b,c\ (a_0)$	0.66540	1.22265
e	0.89223	0.64537

Table 15.216. The energy parameters (eV) of functional groups of aromatics and heterocyclics.

Parameters	$\overset{3e}{C=C}$ Group	CH Group
f_1	0.75	1
n_1	2	1
n_2	0	0
n_3	0	0
C_1	0.5	0.75
C_2	0.85252	1
c_1	1	1
c_2	0.85252	0.91771
c_3	0	1
c_4	3	1
c_5	0	1
C_{1o}	0.5	0.75
C_{2o}	0.85252	1
$V_e\ (eV)$	-101.12679	-37.10024
$V_p\ (eV)$	20.69825	13.17125
$T\ (eV)$	34.31559	11.58941
$V_m\ (eV)$	-17.15779	-5.79470
$E(AO/HO)\ (eV)$	0	-14.63489
$\Delta E_{H_2MO}(AO/HO)\ (eV)$	0	-1.13379

$E_T(AO/HO)\ (eV)$	0	-13.50110
$E_T(H_2MO)\ (eV)$	-63.27075	-31.63539
$E_T(atom-atom,msp^3.AO)\ (eV)$	-2.26759	-0.56690
$E_T(MO)\ (eV)$	-65.53833	-32.20226
$\omega\ (10^{15}\ rad/s)$	49.7272	26.4826
$E_K\ (eV)$	32.73133	17.43132
$\bar{E}_D\ (eV)$	-0.35806	-0.26130
$\bar{E}_{Kvib}\ (eV)$	0.19649 [49]	0.35532 Eq. (13.458)
$\bar{E}_{osc}\ (eV)$	-0.25982	-0.08364
$E_{mag}\ (eV)$	0.14803	0.14803
$E_T(Group)\ (eV)$	-49.54347	-32.28590
$E_{initial}(c_4\ AO/HO)\ (eV)$	-14.63489	-14.63489
$E_{initial}(c_5\ AO/HO)\ (eV)$	0	-13.59844
$E_D(Group)\ (eV)$	5.63881	3.90454

Table 15.215. The MO to HO intercept geometrical bond parameters of benzene. E_T is $E_T\left(atom-atom,msp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)
$C-H\left(CH\right)$	C	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597
$C\overset{3e}{=}HC_a\overset{3e}{=}C$	C_a	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597

Bond	$E_{Coulomb}\left(C2sp^3\right)$(eV) Final	$E\left(C2sp^3\right)$ (eV) Final	θ' $(^\circ)$	θ_1 $(^\circ)$	θ_2 $(^\circ)$	d_1 (a_0)	d_2 (a_0)
$C-H\left(CH\right)$	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$C\overset{3e}{=}HC_a\overset{3e}{=}C$	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533

Table 15.217. The total bond energies of benzene calculated using the functional group composition and the energies of Table 15.216 compared to the experimental values [2].

Formula	Name	$C\overset{3e}{=}C$	CH	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_6H_6	Benzene	6	6	57.26008	57.26340	0.00006

Table 15.218. The bond angle parameters of benzene and experimental values [1]. E_T is $E_T\left(atom-atom,msp^3.AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2
$\angle CCC$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1
$\angle CCH$ (aromatic)											

Atoms of Angle	c_1	c_2'	E_T (eV)	θ_v $(^\circ)$	θ_1 $(^\circ)$	θ_2 $(^\circ)$	Cal. θ $(^\circ)$	Exp. θ $(^\circ)$
$\angle CCC$ (aromatic)	1	0.79232	-1.85836				120.19	120 [50-52] (benzene)
$\angle CCH$ (aromatic)					120.19		119.91	120 [50-52] (benzene)

Table 1.1. The calculated and experimental total bond energies of n-alkanes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_3H_8	Propane	41.46896	41.434	-0.00085
C_4H_{10}	Butane	53.62666	53.61	-0.00036
C_5H_{12}	Pentane	65.78436	65.77	-0.00017
C_6H_{14}	Hexane	77.94206	77.93	-0.00019
C_7H_{16}	Heptane	90.09976	90.09	-0.00013
C_8H_{18}	Octane	102.25746	102.25	-0.00006
C_9H_{20}	Nonane	114.41516	114.40	-0.00012
$C_{10}H_{22}$	Decane	126.57286	126.57	-0.00003
$C_{11}H_{24}$	Undecane	138.73056	138.736	0.00004
$C_{12}H_{26}$	Dodecane	150.88826	150.88	-0.00008
$C_{18}H_{38}$	Octadecane	223.83446	223.85	0.00008

Table 1.2. The calculated and experimental total bond energies of branched alkanes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_4H_{10}	Isobutane	53.69922	53.695	-0.00007
C_5H_{12}	Isopentane	65.85692	65.843	-0.00021
C_5H_{12}	Neopentane	65.86336	65.992	0.00195
C_6H_{14}	2-Methylpentane	78.01462	78.007	-0.00010
C_6H_{14}	3-Methylpentane	78.01462	77.979	-0.00046
C_6H_{14}	2,2-Dimethylbutane	78.02106	78.124	0.00132
C_6H_{14}	2,3-Dimethylbutane	77.99581	78.043	0.00061
C_7H_{16}	2-Methylhexane	90.17232	90.160	-0.00014
C_7H_{16}	3-Methylhexane	90.17232	90.127	-0.00051
C_7H_{16}	3-Ethylpentane	90.17232	90.108	-0.00072
C_7H_{16}	2,2-Dimethylpentane	90.17876	90.276	0.00107
C_7H_{16}	2,2,3-Trimethylbutane	90.22301	90.262	0.00044
C_7H_{16}	2,4-Dimethylpentane	90.24488	90.233	-0.00013
C_7H_{16}	3,3-Dimethylpentane	90.17876	90.227	0.00054
C_8H_{18}	2-Methylheptane	102.33002	102.322	-0.00008
C_8H_{18}	3-Methylheptane	102.33002	102.293	-0.00036
C_8H_{18}	4-Methylheptane	102.33002	102.286	-0.00043
C_8H_{18}	3-Ethylhexane	102.30169	102.274	-0.00027
C_8H_{18}	2,2-Dimethylhexane	102.33646	102.417	0.00079
C_8H_{18}	2,3-Dimethylhexane	102.31121	102.306	-0.00005
C_8H_{18}	2,4-Dimethylhexane	102.40258	102.362	-0.00040
C_8H_{18}	2,5-Dimethylhexane	102.40258	102.396	-0.00006
C_8H_{18}	3,3-Dimethylhexane	102.33646	102.369	0.00032
C_8H_{18}	3,4-Dimethylhexane	102.31121	102.296	-0.00015
C_8H_{18}	3-Ethyl-2-methylpentane	102.31121	102.277	-0.00033
C_8H_{18}	3-Ethyl-3-methylpentane	102.33646	102.317	-0.00019
C_8H_{18}	2,2,3-Trimethylpentane	102.38071	102.370	-0.00010
C_8H_{18}	2,2,4-Trimethylpentane	102.40902	102.412	0.00003
C_8H_{18}	2,3,3-Trimethylpentane	102.38071	102.332	-0.00048
C_8H_{18}	2,3,4-Trimethylpentane	102.29240	102.342	0.00049
C_8H_{18}	2,2,3,3-Tetramethylbutane	102.41632	102.433	0.00016
C_9H_{20}	2,3,5-Trimethylhexane	114.54147	114.551	0.00008
C_9H_{20}	3,3-Diethylpentane	114.49416	114.455	-0.00034
C_9H_{20}	2,2,3,3-Tetramethylpentane	114.57402	114.494	-0.00070
C_9H_{20}	2,2,3,4-Tetramethylpentane	114.51960	114.492	-0.00024

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_9H_{20}	2,2,4,4-Tetramethylpentane	114.57316	114.541	-0.00028
C_9H_{20}	2,3,3,4-Tetramethylpentane	114.58266	114.484	-0.00086
$C_{10}H_{22}$	2-Methylnonane	126.64542	126.680	0.00027
$C_{10}H_{22}$	5-Methylnonane	126.64542	126.663	0.00014

Table 1.3. The calculated and experimental total bond energies of alkenes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_3H_6	Propene	35.56033	35.63207	0.00201
C_4H_8	1-Butene	47.71803	47.78477	0.00140
C_4H_8	trans-2-Butene	47.93116	47.90395	-0.00057
C_4H_8	Isobutene	47.90314	47.96096	0.00121
C_5H_{10}	1-Pentene	59.87573	59.95094	0.00125
C_5H_{10}	trans-2-Pentene	60.08886	60.06287	-0.00043
C_5H_{10}	2-Methyl-1-butene	60.06084	60.09707	0.00060
C_5H_{10}	2-Methyl-2-butene	60.21433	60.16444	-0.00083
C_5H_{10}	3-Methyl-1-butene	59.97662	60.01727	0.00068
C_6H_{12}	1-Hexene	72.03343	72.12954	0.00133
C_6H_{12}	trans-2-Hexene	72.24656	72.23733	-0.00013
C_6H_{12}	trans-3-Hexene	72.24656	72.24251	-0.00006
C_6H_{12}	2-Methyl-1-pentene	72.21854	72.29433	0.00105
C_6H_{12}	2-Methyl-2-pentene	72.37203	72.37206	0.00000
C_6H_{12}	3-Methyl-1-pentene	72.13432	72.19173	0.00080
C_6H_{12}	4-Methyl-1-pentene	72.10599	72.21038	0.00145
C_6H_{12}	3-Methyl-trans-2-pentene	72.37203	72.33268	-0.00054
C_6H_{12}	4-Methyl-trans-2-pentene	72.34745	72.31610	-0.00043
C_6H_{12}	2-Ethyl-1-butene	72.21854	72.25909	0.00056
C_6H_{12}	2,3-Dimethyl-1-butene	72.31943	72.32543	0.00008
C_6H_{12}	3,3-Dimethyl-1-butene	72.31796	72.30366	-0.00020
C_6H_{12}	2,3-Dimethyl-2-butene	72.49750	72.38450	-0.00156
C_7H_{14}	1-Heptene	84.19113	84.27084	0.00095
C_7H_{14}	5-Methyl-1-hexene	84.26369	84.30608	0.00050
C_7H_{14}	trans-3-Methyl-3-hexene	84.52973	84.42112	-0.00129
C_7H_{14}	2,4-Dimethyl-1-pentene	84.44880	84.49367	0.00053
C_7H_{14}	4,4-Dimethyl-1-pentene	84.27012	84.47087	0.00238
C_7H_{14}	2,4-Dimethyl-2-pentene	84.63062	84.54445	-0.00102
C_7H_{14}	trans-4,4-Dimethyl-2-pentene	84.54076	84.54549	0.00006
C_7H_{14}	2-Ethyl-3-methyl-1-butene	84.47713	84.44910	-0.00033
C_7H_{14}	2,3,3-Trimethyl-1-butene	84.51274	84.51129	-0.00002
C_8H_{16}	1-Octene	96.34883	96.41421	0.00068
C_8H_{16}	trans-2,2-Dimethyl-3-hexene	96.69846	96.68782	-0.00011
C_8H_{16}	3-Ethyl-2-methyl-1-pentene	96.63483	96.61113	-0.00025
C_8H_{16}	2,4,4-Trimethyl-1-pentene	96.61293	96.71684	0.00107
C_8H_{16}	2,4,4-Trimethyl-2-pentene	96.67590	96.65880	-0.00018
$C_{10}H_{20}$	1-Decene	120.66423	120.74240	0.00065
$C_{12}H_{24}$	1-Dodecene	144.97963	145.07163	0.00063
$C_{16}H_{32}$	1-Hexadecene	193.61043	193.71766	0.00055

Table 1.4. The calculated and experimental total bond energies of alkynes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_3H_4	Propyne	29.42932	29.40432	-0.00085
C_4H_6	1-Butyne	41.58702	41.55495	-0.00077
C_4H_6	2-Butyne	41.72765	41.75705	0.00070
C_9H_{16}	1-Nonyne	102.37552	102.35367	-0.00021

Table 1.5. The calculated and experimental total bond energies of alkyl fluorides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CF_4	Tetrafluoromethane	21.07992	21.016	-0.00303
CHF_3	Trifluoromethane	19.28398	19.362	0.00405
CH_2F_2	Difluoromethane	18.22209	18.280	0.00314
C_3H_7F	1-Fluoropropane	41.86745	41.885	0.00041
C_3H_7F	2-Fluoropropane	41.96834	41.963	-0.00012

Table 1.6. The calculated and experimental total bond energies of alkyl chlorides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CCl_4	Tetrachloromethane	13.43181	13.448	0.00123
$CHCl_3$	Trichloromethane	14.49146	14.523	0.00217
CH_2Cl_2	Dichloromethane	15.37248	15.450	0.00499
CH_3Cl	Chloromethane	16.26302	16.312	0.00299
C_2H_5Cl	Chloroethane	28.61064	28.571	-0.00138
C_3H_7Cl	1-Chloropropane	40.76834	40.723	-0.00112
C_3H_7Cl	2-Chloropropane	40.86923	40.858	-0.00028
C_4H_9Cl	1-Chlorobutane	52.92604	52.903	-0.00044
C_4H_9Cl	2-Chlorobutane	53.02693	52.972	-0.00104
C_4H_9Cl	1-Chloro-2-methylpropane	52.99860	52.953	-0.00085
C_4H_9Cl	2-Chloro-2-methylpropane	53.21057	53.191	-0.00037
$C_5H_{11}Cl$	1-Chloropentane	65.08374	65.061	-0.00034
$C_5H_{11}Cl$	1-Chloro-3-methylbutane	65.15630	65.111	-0.00069
$C_5H_{11}Cl$	2-Chloro-2-methylbutane	65.36827	65.344	-0.00037
$C_5H_{11}Cl$	2-Chloro-3-methylbutane	65.16582	65.167	0.00002
$C_6H_{13}Cl$	2-Chlorohexane	77.34233	77.313	-0.00038
$C_8H_{17}Cl$	1-Chlorooctane	101.55684	101.564	0.00007
$C_{12}H_{25}Cl$	1-Chlorododecane	150.18764	150.202	0.00009
$C_{18}H_{37}Cl$	1-Chlorooctadecane	223.13384	223.175	0.00018

Table 1.7. The calculated and experimental total bond energies of alkyl bromides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CBr_4	Tetrabromomethane	11.25929	11.196	-0.00566
$CHBr_3$	Tribromomethane	12.87698	12.919	0.00323
CH_3Br	Bromomethane	15.67551	15.732	0.00360
C_2H_5Br	Bromoethane	28.03939	27.953	-0.00308
C_3H_7Br	1-Bromopropane	40.19709	40.160	-0.00093
C_3H_7Br	2-Bromopropane	40.29798	40.288	-0.00024
$C_5H_{10}Br_2$	2,3-Dibromo-2-methylbutane	63.48143	63.477	-0.00007
$C_6H_{13}Br$	1-Bromohexane	76.67019	76.634	-0.00047
$C_7H_{15}Br$	1-Bromoheptane	88.82789	88.783	-0.00051
$C_8H_{17}Br$	1-Bromooctane	100.98559	100.952	-0.00033
$C_{12}H_{25}Br$	1-Bromododecane	149.61639	149.573	-0.00029
$C_{16}H_{33}Br$	1-Bromohexadecane	198.24719	198.192	-0.00028

Table 1.8. The calculated and experimental total bond energies of alkyl iodides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CHI_3	Triiodomethane	10.35888	10.405	0.00444
CH_2I_2	Diiodomethane	12.94614	12.921	-0.00195
CH_3I	Iodomethane	15.20294	15.163	-0.00263
C_2H_5I	Iodoethane	27.36064	27.343	-0.00066
C_3H_7I	1-Iodopropane	39.51834	39.516	-0.00006
C_3H_7I	2-Iodopropane	39.61923	39.623	0.00009
C_4H_9I	2-Iodo-2-methylpropane	51.96057	51.899	-0.00119

Table 1.9. The calculated and experimental total bond energies of alkene halides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_3Cl	Chloroethene	22.46700	22.505	0.00170
C_3H_5Cl	2-Chloropropene	35.02984	35.05482	0.00071

Table 1.10. The calculated and experimental total bond energies of alcohols using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_4O	Methanol	21.11038	21.131	0.00097
C_2H_6O	Ethanol	33.40563	33.428	0.00066
C_3H_8O	1-Propanol	45.56333	45.584	0.00046
C_3H_8O	2-Propanol	45.72088	45.766	0.00098
$C_4H_{10}O$	1-Butanol	57.72103	57.736	0.00026
$C_4H_{10}O$	2-Butanol	57.87858	57.922	0.00074
$C_4H_{10}O$	2-Methyl-1-propananol	57.79359	57.828	0.00060
$C_4H_{10}O$	2-Methyl-2-propananol	58.15359	58.126	-0.00048
$C_5H_{12}O$	1-Pentanol	69.87873	69.887	0.00011

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_5H_{12}O$	2-Pentanol	70.03628	70.057	0.00029
$C_5H_{12}O$	3-Pentanol	70.03628	70.097	0.00087
$C_5H_{12}O$	2-Methyl-1-butananol	69.95129	69.957	0.00008
$C_5H_{12}O$	3-Methyl-1-butananol	69.95129	69.950	-0.00002
$C_5H_{12}O$	2-Methyl-2-butananol	70.31129	70.246	-0.00092
$C_5H_{12}O$	3-Methyl-2-butananol	69.96081	70.083	0.00174
$C_6H_{14}O$	1-Hexanol	82.03643	82.054	0.00021
$C_6H_{14}O$	2-Hexanol	82.19398	82.236	0.00052
$C_7H_{16}O$	1-Heptanol	94.19413	94.214	0.00021
$C_8H_{18}O$	1-Octanol	106.35183	106.358	0.00006
$C_8H_{18}O$	2-Ethyl-1-hexananol	106.42439	106.459	0.00032
$C_9H_{20}O$	1-Nonanol	118.50953	118.521	0.00010
$C_{10}H_{22}O$	1-Decanol	130.66723	130.676	0.00007
$C_{12}H_{26}O$	1-Dodecanol	154.98263	154.984	0.00001
$C_{16}H_{34}O$	1-Hexadecanol	203.61343	203.603	-0.00005

Table 1.11. The calculated and experimental total bond energies of ethers using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_6O	Dimethyl ether	32.84496	32.902	0.00174
C_3H_8O	Ethyl methyl ether	45.19710	45.183	-0.00030
$C_4H_{10}O$	Diethyl ether	57.54924	57.500	-0.00086
$C_4H_{10}O$	Methyl propyl ether	57.35480	57.355	0.00000
$C_4H_{10}O$	Isopropyl methyl ether	57.45569	57.499	0.00075
$C_6H_{14}O$	Dipropyl ether	81.86464	81.817	-0.00059
$C_6H_{14}O$	Disopropyl ether	82.06642	82.088	0.00026
$C_6H_{14}O$	t-Butyl ethyl ether	82.10276	82.033	-0.00085
$C_7H_{16}O$	t-Butyl isopropyl ether	94.36135	94.438	0.00081
$C_8H_{18}O$	Dibutyl ether	106.18004	106.122	-0.00055
$C_8H_{18}O$	Di-sec-butyl ether	106.38182	106.410	0.00027
$C_8H_{18}O$	Di-t-butyl ether	106.36022	106.425	0.00061
$C_8H_{18}O$	t-Butyl isobutyl ether	106.65628	106.497	-0.00218

Table 1.12. The calculated and experimental total bond energies of 1° amines using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_5N	Methylamine	23.88297	23.857	-0.00110
C_2H_7N	Ethylamine	36.04067	36.062	0.00060
C_3H_9N	Propylamine	48.19837	48.243	0.00092
$C_4H_{11}N$	Butylamine	60.35607	60.415	0.00098
$C_4H_{11}N$	sec-Butylamine	60.45696	60.547	0.00148
$C_4H_{11}N$	t-Butylamine	60.78863	60.717	-0.00118
$C_4H_{11}N$	Isobutylamine	60.42863	60.486	0.00094

Table 1.13. The calculated and experimental total bond energies of 2° amines using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_7N	Dimethylamine	35.76895	35.765	-0.00012
$C_4H_{11}N$	Diethylamine	60.22930	60.211	-0.00030
$C_6H_{15}N$	Dipropylamine	84.54470	84.558	0.00016
$C_6H_{15}N$	Diisopropylamine	84.74648	84.846	0.00117
$C_8H_{19}N$	Dibutylamine	108.86010	108.872	0.00011
$C_8H_{19}N$	Diisobutylamine	109.00522	109.106	0.00092

Table 1.14. The calculated and experimental total bond energies of 3° amines using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_3H_9N	Trimethylamine	47.83338	47.761	-0.00152
$C_6H_{15}N$	Triethylamine	84.30648	84.316	0.00012
$C_9H_{21}N$	Tripropylamine	120.77958	120.864	0.00070

Table 1.15. The calculated and experimental total bond energies of aldehydes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_2O	Formaldehyde	15.64628	15.655	0.00056
C_2H_4O	Acetaldehyde	28.18711	28.198	0.00039
C_3H_6O	Propanal	40.34481	40.345	0.00000
C_4H_8O	Butanal	52.50251	52.491	-0.00022
C_4H_8O	Isobutanal	52.60340	52.604	0.00001
$C_5H_{10}O$	Pentanal	64.66021	64.682	0.00034
$C_7H_{14}O$	Heptanal	88.97561	88.942	-0.00038
$C_8H_{16}O$	Octanal	101.13331	101.179	0.00045
$C_8H_{16}O$	2-Ethylhexanal	101.20587	101.259	0.00053

Table 1.16. The calculated and experimental total bond energies of ketones using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_3H_6O	Acetone	40.68472	40.672	-0.00031
C_4H_8O	2-Butanone	52.84242	52.84	-0.00005
$C_5H_{10}O$	2-Pentanone	65.00012	64.997	-0.00005
$C_5H_{10}O$	3-Pentanone	65.00012	64.997	-0.00005
$C_5H_{10}O$	3-Methyl-2-butanone	65.10101	65.036	-0.00099
$C_6H_{12}O$	2-Hexanone	77.15782	77.152	-0.00008
$C_6H_{12}O$	3-Hexanone	77.15782	77.138	-0.00025
$C_6H_{12}O$	2-Methyl-3-pentanone	77.25871	77.225	-0.00043
$C_6H_{12}O$	3,3-Dimethyl-2-butanone	77.29432	77.273	-0.00028
$C_7H_{14}O$	3-Heptanone	89.31552	89.287	-0.00032
$C_7H_{14}O$	4-Heptanone	89.31552	89.299	-0.00018
$C_7H_{14}O$	2,2-Dimethyl-3-pentanone	89.45202	89.458	0.00007

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_7H_{14}O$	2,4-Dimethyl-3-pentanone	89.51730	89.434	-0.00093
$C_8H_{16}O$	2,2,4-Trimethyl-3-pentanone	101.71061	101.660	-0.00049
$C_9H_{18}O$	2-Nonanone	113.63092	113.632	0.00001
$C_9H_{18}O$	5-Nonanone	113.63092	113.675	0.00039
$C_9H_{18}O$	2,6-Dimethyl-4-heptanone	113.77604	113.807	0.00027

Table 1.17. The calculated and experimental total bond energies of carboxylic acids using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_2O_2	Formic acid	21.01945	21.036	0.00079
$C_2H_4O_2$	Acetic acid	33.55916	33.537	-0.00066
$C_3H_6O_2$	Propanoic acid	45.71686	45.727	0.00022
$C_4H_8O_2$	Butanoic acid	57.87456	57.883	0.00015
$C_5H_{10}O_2$	Pentanoic acid	70.03226	69.995	-0.00053
$C_5H_{10}O_2$	3-Methylbutanoic acid	70.10482	70.183	0.00111
$C_5H_{10}O_2$	2,2-Dimethylpropanoic acid	70.31679	69.989	-0.00468
$C_6H_{12}O_2$	Hexanoic acid	82.18996	82.149	-0.00050
$C_7H_{14}O_2$	Heptanoic acid	94.34766	94.347	0.00000
$C_8H_{16}O_2$	Octanoic acid	106.50536	106.481	-0.00022
$C_9H_{18}O_2$	Nonanoic acid	118.66306	118.666	0.00003
$C_{10}H_{20}O_2$	Decanoic acid	130.82076	130.795	-0.00020
$C_{12}H_{24}O_2$	Dodecanoic acid	155.13616	155.176	0.00026
$C_{14}H_{28}O_2$	Tetradecanoic acid	179.45156	179.605	0.00085
$C_{15}H_{30}O_2$	Pentadecanoic acid	191.60926	191.606	-0.00002
$C_{16}H_{32}O_2$	Hexadecanoic acid	203.76696	203.948	0.00089
$C_{18}H_{36}O_2$	Stearic acid	228.08236	228.298	0.00094
$C_{20}H_{40}O_2$	Eicosanoic acid	252.39776	252.514	0.00046

Table 1.18. The calculated and experimental total bond energies of carboxylic acid esters using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_2H_4O_2$	Methyl formate	32.71076	32.762	0.00156
$C_3H_6O_2$	Methyl acetate	45.24849	45.288	0.00087
$C_6H_{12}O_2$	Methyl pentanoate	81.72159	81.726	0.00005
$C_7H_{14}O_2$	Methyl hexanoate	93.87929	93.891	0.00012
$C_8H_{16}O_2$	Methyl heptanoate	106.03699	106.079	0.00040
$C_9H_{18}O_2$	Methyl octanoate	118.19469	118.217	0.00018
$C_{10}H_{20}O_2$	Methyl nonanoate	130.35239	130.373	0.00016
$C_{11}H_{22}O_2$	Methyl decanoate	142.51009	142.523	0.00009
$C_{12}H_{24}O_2$	Methyl undecanoate	154.66779	154.677	0.00006
$C_{13}H_{26}O_2$	Methyl dodecanoate	166.82549	166.842	0.00010
$C_{14}H_{28}O_2$	Methyl tridecanoate	178.98319	179.000	0.00009
$C_{15}H_{30}O_2$	Methyl tetradecanoate	191.14089	191.170	0.00015
$C_{16}H_{32}O_2$	Methyl pentadecanoate	203.29859	203.356	0.00028
$C_4H_8O_2$	Propyl formate	57.76366	57.746	-0.00030
$C_4H_8O_2$	Ethyl acetate	57.63888	57.548	-0.00157
$C_5H_{10}O_2$	Isopropyl acetate	69.89747	69.889	-0.00013
$C_5H_{10}O_2$	Ethyl propanoate	69.79658	69.700	-0.00139
$C_6H_{12}O_2$	Butyl acetate	81.95428	81.873	-0.00099
$C_6H_{12}O_2$	t-Butyl acetate	82.23881	82.197	-0.00051

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_6H_{12}O_2$	Methyl 2,2-dimethylpropanoate	82.00612	81.935	-0.00087
$C_7H_{14}O_2$	Ethyl pentanoate	94.11198	94.033	-0.00084
$C_7H_{14}O_2$	Ethyl 3-methylbutanoate	94.18454	94.252	0.00072
$C_7H_{14}O_2$	Ethyl 2,2-dimethylpropanoate	94.39651	94.345	-0.00054
$C_8H_{16}O_2$	Isobutyl isobutanoate	106.44313	106.363	-0.00075
$C_8H_{16}O_2$	Propyl pentanoate	106.26968	106.267	-0.00003
$C_8H_{16}O_2$	Isopropyl pentanoate	106.37057	106.384	0.00013
$C_9H_{18}O_2$	Butyl pentanoate	118.42738	118.489	0.00052
$C_9H_{18}O_2$	sec-Butyl pentanoate	118.52827	118.624	0.00081
$C_9H_{18}O_2$	Isobutyl pentanoate	118.49994	118.576	0.00064

Table 1.19. The calculated and experimental total bond energies of amides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_3NO	Formamide	23.68712	23.697	0.00041
C_2H_5NO	Acetamide	36.15222	36.103	-0.00135
C_3H_7NO	Propanamide	48.30992	48.264	-0.00094
C_4H_9NO	Butanamide	60.46762	60.449	-0.00030
C_4H_9NO	2-Methylpropanamide	60.51509	60.455	-0.00099
$C_5H_{11}NO$	Pentanamide	72.62532	72.481	-0.00200
$C_5H_{11}NO$	2,2-Dimethylpropanamide	72.67890	72.718	0.00054
$C_6H_{13}NO$	Hexanamide	84.78302	84.780	-0.00004
$C_8H_{17}NO$	Octanamide	109.09842	109.071	-0.00025

Table 1.20. The calculated and experimental total bond energies of N-alkyl and N,N-dialkyl amides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_3H_7NO	N,N-Dimethylformamide	47.53142	47.574	0.00090
C_4H_9NO	N,N-Dimethylacetamide	59.91404	59.890	-0.00041
$C_6H_{13}NO$	N-Butylacetamide	84.63649	84.590	-0.00055

Table 1.21. The calculated and experimental total bond energies of urea using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_4N_2O	Urea	31.35919	31.393	0.00108

Table 1.22. The calculated and experimental total bond energies of acid halide using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_3ClO	Acetyl chloride	28.02174	27.990	-0.00115

Table 1.23. The calculated and experimental total bond energies of acid anhydrides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_4H_6O_3$	Acetic anhydride	56.94096	56.948	0.00013
$C_6H_{10}O_3$	Propanoic anhydride	81.25636	81.401	0.00177

Table 1.24. The calculated and experimental total bond energies of nitriles using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_3N	Acetonitrile	25.72060	25.77	0.00174
C_3H_5N	Propanenitrile	37.87830	37.94	0.00171
C_4H_7N	Butanenitrile	50.03600	50.08	0.00082
C_4H_7N	2-Methylpropanenitrile	50.13689	50.18	0.00092
C_5H_9N	Pentanenitrile	62.19370	62.26	0.00111
C_5H_9N	2,2-Dimethylpropanenitrile	62.47823	62.40	-0.00132
$C_7H_{13}N$	Heptanenitrile	86.50910	86.59	0.00089
$C_8H_{15}N$	Octanenitrile	98.66680	98.73	0.00069
$C_{10}H_{19}N$	Decanenitrile	122.98220	123.05	0.00057
$C_{14}H_{27}N$	Tetradecanenitrile	171.61300	171.70	0.00052

Table 1.25. The calculated and experimental total bond energies of thiols using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
HS	Hydrogen Sulfide	3.77430	3.653	-0.03320
H_2S	Dihydrogen Sulfide	7.56058	7.605	0.00582
CH_4S	Methanethiol	19.60264	19.575	-0.00141
C_2H_6S	Ethanethiol	31.76034	31.762	0.00005
C_3H_8S	1-Propanethiol	43.91804	43.933	0.00035
C_3H_8S	2-Propanethiol	44.01893	44.020	0.00003
$C_4H_{10}S$	1-Butanethiol	56.07574	56.089	0.00024
$C_4H_{10}S$	2-Butanethiol	56.17663	56.181	0.00009
$C_4H_{10}S$	2-Methyl-1-propanethiol	56.14830	56.186	0.00066
$C_4H_{10}S$	2-Methyl-2-propanethiol	56.36027	56.313	-0.00084
$C_5H_{12}S$	2-Methyl-1-butanethiol	68.30600	68.314	0.00012
$C_5H_{12}S$	1-Pentanethiol	68.23344	68.264	0.00044
$C_5H_{12}S$	2-Methyl-2-butanethiol	68.51797	68.441	-0.00113
$C_5H_{12}S$	3-Methyl-2-butanethiol	68.31552	68.381	0.00095
$C_5H_{12}S$	2,2-Dimethyl-1-propanethiol	68.51797	68.461	-0.00084
$C_6H_{14}S$	1-Hexanethiol	80.39114	80.416	0.00031
$C_6H_{14}S$	2-Methyl-2-pentanethiol	80.67567	80.607	-0.00085
$C_6H_{14}S$	2,3-Dimethyl-2-butanethiol	80.71992	80.603	-0.00145
$C_7H_{16}S$	1-Heptanethiol	92.54884	92.570	0.00023
$C_{10}H_{22}S$	1-Decanethiol	129.02194	129.048	0.00020

Table 1.26. The calculated and experimental total bond energies of sulfides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_6S	Dimethyl sulfide	31.65668	31.672	0.00048
C_3H_8S	Ethyl methyl sulfide	43.81438	43.848	0.00078
$C_4H_{10}S$	Diethyl sulfide	55.97208	56.043	0.00126
$C_4H_{10}S$	Methyl propyl sulfide	55.97208	56.029	0.00102
$C_4H_{10}S$	Isopropyl methyl sulfide	56.07297	56.115	0.00075
$C_5H_{12}S$	Butyl methyl sulfide	68.12978	68.185	0.00081
$C_5H_{12}S$	t-Butyl methyl sulfide	68.28245	68.381	0.00144
$C_5H_{12}S$	Ethyl propyl sulfide	68.12978	68.210	0.00117
$C_5H_{12}S$	Ethyl isopropyl sulfide	68.23067	68.350	0.00174
$C_6H_{14}S$	Diisopropyl sulfide	80.48926	80.542	0.00065
$C_6H_{14}S$	Butyl ethyl sulfide	80.28748	80.395	0.00133
$C_6H_{14}S$	Methyl pentyl sulfide	80.28748	80.332	0.00056
$C_8H_{18}S$	Dibutyl sulfide	104.60288	104.701	0.00094
$C_8H_{18}S$	Di-sec-butyl sulfide	104.80466	104.701	-0.00099
$C_8H_{18}S$	Di-t-butyl sulfide	104.90822	104.920	0.00011
$C_8H_{18}S$	Diisobutyl sulfide	104.74800	104.834	0.00082
$C_{10}H_{22}S$	Ethyl propyl sulfide	128.91828	128.979	0.00047
$C_{10}H_{22}S$	Diisopentyl sulfide	129.06340	129.151	0.00068

Table 1.27. The calculated and experimental total bond energies of disulfides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_2H_6S_2$	Dimethyl disulfide	34.48127	34.413	-0.00199
$C_4H_{10}S_2$	Diethyl disulfide	58.79667	58.873	0.00129
$C_6H_{14}S_2$	Dipropyl disulfide	83.11207	83.169	0.00068
$C_8H_{18}S_2$	Di-t-butyl disulfide	107.99653	107.919	-0.00072

Table 1.28. The calculated and experimental total bond energies of sulfoxides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_6SO	Dimethyl sulfoxide	35.52450	35.435	-0.00253
$C_4H_{10}SO$	Diethyl sulfoxide	59.83990	59.891	0.00085
$C_6H_{14}SO$	Dipropyl sulfoxide	84.15530	84.294	0.00165

Table 1.29. The calculated and experimental total bond energies of sulfones using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_2H_6SO_2$	Dimethyl sulfone	40.27588	40.316	0.00100

Table 1.30. The calculated and experimental total bond energies of sulfites using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_2H_6SO_3$	Dimethyl sulfite	43.95058	44.042	0.00207
$C_4H_{10}SO_3$	Diethyl sulfite	68.54939	68.648	0.00143
$C_8H_{18}SO_3$	Dibutyl sulfite	117.18019	117.191	0.00009

Table 1.31. The calculated and experimental total bond energies of sulfates using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_2H_6SO_4$	Dimethyl sulfate	48.70617	48.734	0.00058
$C_4H_{10}SO_4$	Diethyl sulfate	73.30077	73.346	0.00061
$C_6H_{14}SO_4$	Dipropyl sulfate	97.61617	97.609	-0.00008

Table 1.32. The calculated and experimental total bond energies of nitro alkanes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_3NO_2	Nitromethane	25.14934	25.107	-0.00168
$C_2H_5NO_2$	Nitroethane	37.30704	37.292	-0.00040
$C_3H_7NO_2$	1-Nitropropane	49.46474	49.451	-0.00028
$C_3H_7NO_2$	2-Nitropropane	49.56563	49.602	0.00074
$C_4H_9NO_2$	1-Nitrobutane	61.62244	61.601	-0.00036
$C_4H_9NO_2$	2-Nitroisobutane	61.90697	61.945	0.00061
$C_5H_{11}NO_2$	1-Nitropentane	73.78014	73.759	-0.00028

Table 1.33. The calculated and experimental total bond energies of nitrite using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_3NO_2	Methyl nitrite	24.92328	24.955	0.00126

Table 1.34. The calculated and experimental total bond energies of nitrate using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_3NO_3	Methyl nitrate	28.18536	28.117	-0.00244
$C_2H_5NO_3$	Ethyl nitrate	40.34306	40.396	0.00131
$C_3H_7NO_3$	Propyl nitrate	52.50076	52.550	0.00093
$C_3H_7NO_3$	Isopropyl nitrate	52.60165	52.725	0.00233

Table 1.35. The calculated and experimental total bond energies of conjugated alkenes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_5H_8	Cyclopentene	54.83565	54.86117	0.00047
C_4H_6	1,3 Butadiene	42.09159	42.12705	0.00084
C_5H_8	1,3 Pentadiene	54.40776	54.42484	0.00031
C_5H_8	1,4 Pentadiene	54.03745	54.11806	0.00149
C_5H_6	1,3 Cyclopentadiene	49.27432	49.30294	0.00058

Table 1.36. The calculated and experimental total bond energies of aromatics and heterocyclic aromatics using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_6H_6	Benzene	57.26008	57.26340	0.00006
C_6H_5Cl	Chlorobenzene	56.55263	56.581	0.00051
$C_6H_4Cl_2$	m-dichlorobenzene	55.84518	55.852	0.00012
$C_6H_3Cl_3$	1,2,3-trichlorobenzene	55.13773	55.077	-0.00111
$C_6H_3Cl_3$	1,3,5-trichlorbenzene	55.29542	55.255	-0.00073
C_6Cl_6	Hexachlorobenzene	52.57130	52.477	-0.00179
$C_6H_5NO_2$	Nitrobenzene	65.18754	65.217	0.00046
C_7H_8	Toluene	69.48425	69.546	0.00088
$C_7H_6O_2$	Benzoic acid	73.76938	73.762	-0.00009
$C_7H_5ClO_2$	2-chlorobenzoic acid	73.06193	73.082	0.00027
$C_7H_5ClO_2$	3-chlorobenzoic acid	73.26820	73.261	-0.00010
$C_7H_5ClO_2$	4-chlorobenzoic acid	73.26820	73.247	-0.00028
C_6H_7N	Aniline	64.43373	64.374	-0.00093
C_7H_9N	2-methylaniline	76.62345	76.643	-0.00025
C_7H_9N	3-methylaniline	76.62345	76.661	0.00050
C_7H_9N	4-methylaniline	76.62345	76.654	0.00040
$C_6H_6N_2O_2$	2-nitroaniline	72.47476	72.424	-0.00070
$C_6H_6N_2O_2$	3-nitroaniline	72.47476	72.481	-0.00009
$C_6H_6N_2O_2$	4-nitroaniline	72.47476	72.476	-0.00002
$C_7H_7NO_2$	Aniline-2-carboxylic acid	80.90857	80.941	0.00041
$C_7H_7NO_2$	Aniline-3-carboxylic acid	80.90857	80.813	-0.00118
$C_7H_7NO_2$	Aniline-4-carboxylic acid	80.90857	80.949	0.00050
C_6H_6O	Phenol	61.75817	61.704	-0.00087
$C_6H_4N_2O_5$	2,4-dinitrophenol	77.61308	77.642	0.00037
C_6H_8O	Anisole	73.39006	73.355	-0.00047
$C_{10}H_8$	Naphthalene	90.74658	90.79143	0.00049
C_4H_5N	Pyrrole	44.81090	44.785	-0.00057
C_4H_4O	Furan	41.67782	41.692	0.00033
C_4H_4S	Thiophene	40.42501	40.430	0.00013
$C_3H_4N_2$	Imidazole	39.76343	39.74106	-0.00056
C_5H_5N	Pyridine	51.91802	51.87927	-0.00075
$C_4H_4N_2$	Pyrimidine	46.57597	46.51794	-0.00125
$C_4H_4N_2$	Pyrazine	46.57597	46.51380	0.00095
C_9H_7N	Quinoline	85.40453	85.48607	0.00178
C_9H_7N	Isoquinoline	85.40453	85.44358	0.00046
C_8H_7N	Indole	78.52215	78.514	-0.00010
$C_5H_5N_5$	Adenine	70.83735	70.79811	-0.00055

REFERENCES FOR SECTION IV

1. D. R. Lide, *CRC Handbook of Chemistry and Physics*, 86th Edition, CRC Press, Taylor & Francis, Boca Raton, (2005-6), pp. 9-19 to 9-45.
2. G. Herzberg, *Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand Reinhold Company, New York, New York, (1945), p. 344.
3. D. R. Lide, *CRC Handbook of Chemistry and Physics*, 86th Edition, CRC Press, Taylor & Francis, Boca Raton, (2005-6), pp. 9-63; 9-64 to 9-76.
4. R. J. Fessenden, J. S. Fessenden, *Organic Chemistry*, Willard Grant Press. Boston, Massachusetts, (1979), p. 320.
5. cyclohexane at http://webbook.nist.gov/.
6. G. Herzberg, *Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand Reinhold Company, New York, New York, (1945), p. 326.
7. b1 2-methyl-1-propene at http://webbook.nist.gov/.
8. a1 2-methyl-1-propene at http://webbook.nist.gov/.
9. 2-butyne at http://webbook.nist.gov/.
10. trifluoromethane at http://webbook.nist.gov/.
11. fluoroethane at http://webbook.nist.gov/.
12. G. Herzberg, *Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules*, Krieger Publishing Company, Malabar, FL, (1991), p. 195.
13. chloromethane at http://webbook.nist.gov/.
14. methyl bromide at http://webbook.nist.gov/.
15. tetrabromomethane at http://webbook.nist.gov/.
16. methyl iodide at http://webbook.nist.gov/.
17. K. P. Huber, G. Herzberg, *Molecular Spectra and Molecular Structure, IV. Constants of Diatomic Molecules*, Van Nostrand Reinhold Company, New York, (1979).
18. J. Crovisier, Molecular Database—Constants for molecules of astrophysical interest in the gas phase: photodissociation, microwave and infrared spectra, Ver. 4.2, Observatoire de Paris, Section de Meudon, Meudon, France, May 2002, pp. 34–37, available at http://wwwusr.obspm.fr/~crovisie/.
19. methanol at http://webbook.nist.gov/.

20. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, The *Handbook of Infrared and Raman Frequencies of Organic Molecules*, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 46.

21. dimethyl ether at http://webbook.nist.gov/.

22. T. Amano, P. F. Bernath, R. W. McKellar, "Direct observation of the ν_1 and ν_3 fundamental bands of NH_2 by difference frequency laser spectroscopy", J. Mol. Spectrosc., Vol. 94, (1982), pp. 100-113.

23. methylamine at http://webbook.nist.gov/.

24. D. R. Lide, *CRC Handbook of Chemistry and Physics*, 79th Edition, CRC Press, Boca Raton, Florida, (1998-9), pp. 9-80 to 9-85.

25. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, The *Handbook of Infrared and Raman Frequencies of Organic Molecules*, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 482.

26. acetaldehyde at http://webbook.nist.gov/.

27. acetone at http://webbook.nist.gov/.

28. 2-butanone at http://webbook.nist.gov/.

29. acetic acid at http://webbook.nist.gov/.

30. formic acid at http://webbook.nist.gov/.

31. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, The *Handbook of Infrared and Raman Frequencies of Organic Molecules*, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 138.

32. methyl formate at http://webbook.nist.gov/.

33. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, The *Handbook of Infrared and Raman Frequencies of Organic Molecules*, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 144.

34. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, The *Handbook of Infrared and Raman Frequencies of Organic Molecules*, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 147.

35. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, The *Handbook of Infrared and Raman Frequencies of Organic Molecules*, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 143.

36. H. J. Vledder, F. C. Mijlhoff, J. C. Leyte, C. Romers, "An electron diffraction investigation of the molecular structure of gaseous acetic anhydride", Journal of Molecular Structure, Vol. 7, Issues 3-4, (1971), pp. 421-429.

37. acetonitrile at http://webbook.nist.gov/.

38. D. R. Lide, *CRC Handbook of Chemistry and Physics*, 86th Edition, CRC Press, Taylor & Francis, Boca Raton, (2005-6), pp. 10-202 to 10-204.

39. D. R. Lide, *CRC Handbook of Chemistry and Physics*, 86th Edition, CRC Press, Taylor & Francis, Boca Raton, (2005-6), p. 9-79.

40. D. R. Lide, *CRC Handbook of Chemistry and Physics*, 86th Edition, CRC Press, Taylor & Francis, Boca Raton, (2005-6), pp. 9-82 to 9-86.

41. thiirane at http://webbook.nist.gov/.

42. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, The *Handbook of Infrared and Raman Frequencies of Organic Molecules*, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 242.

43. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, The *Handbook of Infrared and Raman Frequencies of Organic Molecules*, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 241.

44. R. M. Ibberson, M. T. F. Telling, S. Parsons, "Structural determination and phase transition behavior of dimethyl sulfate", Acta. Cryst., Vol. B62, (2006), pp. 280-286.

45. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, The *Handbook of Infrared and Raman Frequencies of Organic Molecules*, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 181.

46. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, The *Handbook of Infrared and Raman Frequencies of Organic Molecules*, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 480.

47. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, The *Handbook of Infrared and Raman Frequencies of Organic Molecules*, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 187.

48. 1,3-butadiene at http://webbook.nist.gov/.

49. G. Herzberg, *Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand Reinhold Company, New York, New York, (1945), pp. 362-369.

50. W. I. F. David, R. M. Ibberson, G. A. Jeffrey, J. R. Ruble, "The structure analysis of deuterated benzene and deuterated nitromethane by pulsed-neutron powder diffraction: a comparison with single crystal neutron analysis", Physica B (1992), 180 & 181, pp. 597-600..

51. G. A. Jeffrey, J. R. Ruble, R. K. McMullan, J. A. Pople, "The crystal structure of deuterated benzene," Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences, Vol. 414, No. 1846, (Nov. 9, 1987), pp. 47-57.

52. H. B. Burgi, S. C. Capelli, "Getting more out of crystal-structure analyses," Helvetica Chimica Acta, Vol. 86, (2003), pp. 1625-1640.

53. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, The *Handbook of Infrared and Raman Frequencies of Organic Molecules*, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 481.

54. R. Boese, D. Blaser, M. Nussbaumer, T. M. Krygowski, "Low temperature crystal and molecular structure of nitrobenzene", Structural Chemistry, Vol. 3, No. 5, (1992), pp. 363-368.

55. G. A. Sim, J. M. Robertson, T. H. Goodwin, "The crystal and molecular structure of benzoic acid", Acta Cryst., Vol. 8, (1955), pp.157-164

56. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, The *Handbook of Infrared and Raman Frequencies of Organic Molecules*, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 301.

57. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, The *Handbook of Infrared and Raman Frequencies of Organic Molecules*, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 303.

58. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, The *Handbook of Infrared and Raman Frequencies of Organic Molecules*, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 207.

59. S. Martinez-Carrera, "The crystal structure of Imidazole at -150°C", Acta. Cryst., Vol. 20, (1966), pp. 783-789.

60. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, The *Handbook of Infrared and Raman Frequencies of Organic Molecules*, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), pp. 296-297.

61. H. Sternglanz, C. E. Bugg, "Conformations of N^6-monosubstituted adenine derivatives crystal structure of N^6-methyladenine", Biochimica et Biophysica Acta, Vol. 308, (1973), pp. 1-8.

Section V1

Software Program

The present invention relates to a system of computing and rendering the nature of at least one specie selected from a group of diatomic molecules having at least one atom that is other than hydrogen, polyatomic molecules, molecular ions, polyatomic molecular ions, or molecular radicals, or any functional group therein, comprising physical, Maxwellian solutions of charge, mass, and current density functions of said specie, said system comprising: processing means for processing physical, Maxwellian equations representing charge, mass, and current density functions of said specie; and an output device in communication with the processing means for displaying said physical, Maxwellian solutions of charge, mass, and current density functions of said specie.

In one embodiment, for example, the system comprises five components: (1) the graphical user interface (GUI); (2) the routine for parsing between an input chemical structure or name and taking the input and activating a routine to call up the parts of the molecule (functional groups), which are used for determining the energies and structure to be rendered; (3) the functional-group data base that has an organization of the theoretical solutions; (4) the rendering engine, which calculates and enables manipulations of the image, such as a three-dimensional model in response to commands, as well as responds to commands for data parameters corresponding to the image such as bond energies and charge distribution and geometrical parameters; and (5) data transfer system for inputting numerical data into or out of the computational components and storage components of the main system. The system further comprises spreadsheets with solutions of the bond parameters with output in any standard spreadsheet format. The system also comprises a data-handling program to transfer data from the spreadsheets into the main program.

The output may be, for example, at least one of graphical, simulation, text, and numerical data. The output may be the calculation of at least one of: (1) a bond distance between two atoms; (2) a bond angle between three of the atoms; (3) a bond energy between two atoms; (4) orbital intercept distances and angles; and (5) charge-density functions of atomic, hybridized, and molecular orbitals, wherein the bond distance, bond angle, and bond energy are calculated from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration.

In other embodiments, the charge, current, energy, and geometrical parameters are output to be inputs to other programs that may be used in further applications. For example, the data of heats of formation may be input to another program to be used to predict stability (existence of compounds) equilibrium constants and to predict synthetic pathways. That is, a novel composition of matter may be discovered by calculating at least one of a bond distance between two of the atoms, a bond angle between three of the atoms, and a bond energy between two of the atoms, orbital intercept distances and angles, charge-density functions of atomic, hybridized, and molecular orbitals, the bond distance, bond angle, and bond energy being calculated from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration. The charge and current density functions may be used to predict the electric and magnetic fields of the species to determine other properties due to the interaction of the fields between species. These fields and the predictions of field interactions may be computed using Maxwell's equations. In one embodiment, finite-element analysis is used to predict or calculate the interaction and resulting properties, such as the freezing point, boiling point, density, viscosity, and refractive index. Furthermore, the output data can be used to give thermodynamic, spectroscopic, and other properties, aid in drug design and other applications with or without direct visualization. Furthermore, the data can be input into other programs of the system, which calculate thermodynamic and other properties, or performs a simulation, such as a chemical reaction or molecular dynamics.

The output data may be used to predict a composition of matter comprising a plurality of atoms, the improvement comprising a novel property or use discovered by calculation of at least one of a bond distance between two of the atoms, a bond angle between three of the atoms, and a bond energy between two of the atoms, orbital intercept distances and angles, charge-density functions of atomic, hybridized, and molecular orbitals, the bond distance, bond angle, and bond energy being calculated from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration. The novel property, for example, may be a new pharmaceutical use, or stability at room temperature of a novel arrangement of atoms or ions.

In one embodiment, the output device of the system is a display that displays at least one of visual or graphical media. The display may be at least one of static or dynamic. At least one of vibration, rotation, and translation may be displayed. The displayed information

may be used for at least one of modeling reactivity, predicting physical properties, and aiding in drug and material design. The output device may be a monitor, video projector, printer, or one-, two- or three-dimensional rendering device. The displayed information may be used to model other molecules and provides utility to anticipate their reactivity and physical properties. Additionally, data may be output and used in the same and additional applications as the rendered models and representations of the calculated physical solutions. The processing means of the system may be a general-purpose computer. The general-purpose computer may comprise a central processing unit (CPU), one or more specialized processors, system memory, a mass storage device such as a magnetic disk, an optical disk, or other storage device, an input means. The input means may comprise a serial port, USB port, microphone input, camera input, keyboard or mouse. The processing means comprises a special purpose computer or other hardware system. The system may comprise computer program products such as computer readable medium having embodied therein program code means. The computer readable media may be any available media which can be accessed by a general purpose or special purpose computer. The computer readable media may comprise, for example, at least one of RAM, ROM, EPROM, CD ROM, DVD or other optical disk storage, magnetic disk storage or other magnetic storage devices, or any other medium that can embody the desired program code means and which can be accessed by a general purpose or special purpose computer. The program code means may comprise executable instructions and data, which cause a general purpose computer or special purpose computer to perform a certain function of a group of functions. Commercial examples of suitable program language includes, for example, C++, C, JAVA, FORTRAN, Python and Assembly Languages, programmed with an algorithm based on the physical solutions, and the computer may be a PC, mainframe, supercomputer, or cluster of computers. Commercial examples of suitable programs include, for example, APIs like OpenGL, DirectX, FOX GUI toolkit, and Qt. This program may be developed to run on at least one of operating systems like Windows XP, Windows 2000, Windows Vista, MAC OS, MAC OS X, Linux, Unix, Irix and other Unix-type operating systems.

Millsian software is designed to render 3-D models of molecules, molecular ions, molecular radicals, functional groups thereof, and related structure and property information and produce useful data output and application of the parameters of these species, wherein the nature of their bound electrons and chemical bonds are solved using Dr. Randell L. Mills' Classical Quantum Mechanics theory described in the reference: R. L. Mills, "The Grand Unified Theory of Classical Quantum Mechanics", June 2006 Edition, Cadmus Professional

Communications-Science Press Division, Ephrata, PA, ISBN 0963517171, Library of Congress Control Number 2005936834; posted at http://www.blacklightpower.com/bookdownload.shtml, which is incorporated by this reference in its entirety. Figure 76 provides a flow chart diagram, which is an example of a software system that can be utilized for this purpose, which example is not intended to limit the scope of the disclosed inventions. The main parts of this exemplary software system illustrated in Figure 76 will now be further explained:

Start: A user can start the program by running an executable program file. That might be done, for example, by double clicking the program icon on a Windows-based operating system, or typing the name of the executable file on the command line and pressing the 'Enter' key on a Linux or Unix operating system. The program initially starts by reading data files located in specific directories. The names of those directories and locations are fixed according to the type and format of the data files.

Data files: There are two types of data files used in the software system: functional group data files and molecule data files. Functional group data files contain information about various functional groups. Functional groups are the basic bonding elements or units that each typically comprise an atom, or at least two atoms bound together as found within a molecule (e.g. -Cl , C=C, C=O, CH3). Functional groups typically dictate or define properties and structure of the molecule. Similar functional groups in different molecules typically react in similar ways when subjected to a particular set of reaction conditions. Molecule data files contain information about molecules, molecular ions, and molecular radicals. These data files are processed according to their file formats.

File formats: Millsian software employs two kinds of file formats for storing information about the structure, energies and names of molecules and functional groups: raw-data format and hierarchical format. In a raw-data file, all information is stored as is, below the header describing the type of information. As shown in the Table below, for example, the names of the molecule or functional group are listed below the #NAMES header. The names and positions of the atoms are listed below the #ATOMS header, and so on.

```
#NAMES
CH3
Alkane CH3

#SMILES
C-

#ATOMS
1       C       0       0       0
2       H       1.9775 -0.698 0
3       H       -0.9888         -0.698 1.712
4       H       -0.9888         -0.698 -1.712

#AO
1       1 1s    0.171   2
2       1 2sp3  0.864   -1

#BONDS
1       1 2     1       1.649
2       1 3     1       1.649
3       1 4     1       1.649

#BONDAXES
1       1       1       90      0       0

#DATA
RCH bond angle: 109.44°
CH bond length: 2.097 a
HFORM: 12.492
```

Most of the functional groups files and some simple molecule files are stored in raw data format. The other file format used with the Millsian software system, the hierarchical file format, represents the information in a graph style, in which nodes are connected to other nodes through links. This format is designed to construct molecules by attaching different functional groups in a desired manner. Using this file format, the user can construct complex molecules built from solved functional groups.

For example, as shown in the Table below, the pentane data file includes a #GROUPS header below which is list all of the functional groups that form a part of the pentane molecule. Under the #GROUP_LINKS header is information about how these functional groups are connected to each other to construct pentane.

```
#NAMES
Pentane

#SMILES
CCCCC

#GROUPS
1       C-
2       -C-
3       -C-
4       -C-
5       C-


#GROUP_LINKS
1       1 1     2 1     180
2       2 2     3 1     180
3       3 2     4 1     180
4       4 2     5 1     180
```

Processing data files: As further shown in the flow diagram of Figure 76 for the exemplary Millsian software system, the program first processes the functional group data file and constructs the functional-group objects, which are complete 3-D representations of the functional groups and their related information supplied in the corresponding file. These objects are then ready to be visually displayed through use of a molecule viewer. Next, the program processes the molecule data file. If the molecule date file is in raw-data format, then the program makes a molecule object directly from it. If the file is in hierarchical format, then the program calculates geometric parameters from listed functional groups. The program stores all functional-group objects and molecule objects using internal data structures.

Visualization/ User Interactions: As shown in Figures 77 and 78, the molecule viewer displays the functional-group objects and molecule objects and provides basic interaction capabilities with the displayed objects, such as rotating, scaling, and moving the objects. The molecule viewer also provides other visualization options, such as viewing molecules in wire frame mode, viewing coordinate axes, and changing of the transparency and lighting. The user, for example, can also select parts of a molecule for visualization, like a nucleus, atomic orbital, molecular orbital, or bond axis. The viewer also includes a drop down information window, which provides, for example, related information about molecules, such as bond angles, component functional groups, and total heat of formation. In one embodiment, a user can create new molecules by joining functional groups. For this purpose, the user can select a

first functional group. Next, the user can select an open bond from the functional group where the user desires to attach another group. Next, the user can select another or the same functional group, followed by selecting an open bond from the other group. The user can join the two selected functional groups at the selected open bonds by clicking on 'Join Groups'. This method of joining functional groups at open bonds can be repeated to form the desired molecule.

SMILES input: The Simplified Molecular Input Line Entry Specification or SMILES is a specification for unambiguously describing the structure of chemical molecules using short ASCII strings. Through the user interface, a user can enter SMILES to construct molecules, provided the new molecule comprises functional groups that are in the database. Once a SMILES is entered, a parser reads in and breaks it down into component functional groups. The software system then attaches the component functional groups to create the new molecule object, which can then be viewed using the molecule viewer.

While the claimed invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one of ordinary skill in the art that various changes and modifications can be made to the claimed invention without departing from the spirit and scope thereof.

CONTINUOUS-CHAIN ALKANES (C_nH_{2n+2}, $n = 3,4,5...\infty$)

The continuous-chain alkanes, C_nH_{2n+2}, are the homologous series comprising terminal methyl groups at each end of the chain with $n-2$ methylene (CH_2) groups in between:

$$CH_3\left(CH_2\right)_{n-2}CH_3 \tag{15.109}$$

C_nH_{2n+2} can be solved using the same principles as those used to solve ethane and ethylene wherein the $2s$ and $2p$ shells of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. Three H AOs combine with three carbon $2sp^3$ HOs and two H AOs combine with two carbon $2sp^3$ HOs to form each methyl and methylene group, respectively, where each bond comprises a H_2-type MO developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section. The CH_3 and CH_2 groups bond by forming H_2-type MOs between the remaining $C2sp^3$ HOs on the carbons such that each carbon forms four bonds involving its four $C2sp^3$ HOs. For the alkyl $C-C$ group, $E_T\left(atom-atom, msp^3.AO\right)$ is $-1.85836\ eV$ where both energy contributions are given by Eq. (14.513). It is based on the energy match between the $C2sp^3$ HOs of the chain comprising methylene groups and terminal methyl groups.

The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of straight-chain alkanes are given in Tables 15.4, 15.5, and 15.6, respectively. The total energy of each straight-chain alkane given in Table 15.7 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.6 corresponding to functional-group composition of the molecule. The bond angle parameters of straight-chain alkanes determined using Eqs. (15.79-15.108) are given in Table 15.8. In this angle table and those given in subsequent sections when c_2' is given as the ratio of two values of c_2 designated to Atom 1 and Atom 2 and corresponding to $E_{Coulombic}$ of Atom 1 and Atom 2, respectively, then $c_2' = \dfrac{c_2\left(Atom\ 2\right)}{c_2\left(Atom\ 1\right)}$.

Table 15.4. The geometrical bond parameters of straight-chain alkanes and experimental values [1].

Parameter	$C-C$ Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group
$a\ (a_0)$	2.12499	1.64920	1.67122
$c'\ (a_0)$	1.45744	1.04856	1.05553
Bond Length $2c'$ (Å)	1.54280	1.10974	1.11713
Exp. Bond Length (Å)	1.532 (propane) 1.531 (butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)
$b,c\ (a_0)$	1.54616	1.27295	1.29569
e	0.68600	0.63580	0.63159

Table 15.5. The MO to HO intercept geometrical bond parameters of straight-chain alkanes. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C-H\ (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$H_3C_a-C_bH_2CH_2$	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_a-C_bH_2CH_2$	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117

Table 15.6. The energy parameters (eV) of functional groups of straight-chain alkanes.

Parameters	$C-C$ Group	CH_3 Group	CH_2 Group
n_1	1	3	2
n_2	0	2	1
n_3	0	0	0
C_1	0.5	0.75	0.75
C_2	1	1	1
c_1	1	1	1
c_2	0.91771	0.91771	0.91771
c_3	0	0	1
c_4	2	1	1
c_5	0	3	2
C_{1o}	0.5	0.75	0.75
C_{2o}	1	1	1
$V_e\ (eV)$	-28.79214	-107.32728	-70.41425
$V_p\ (eV)$	9.33352	38.92728	25.78002
$T\ (eV)$	6.77464	32.53914	21.06675
$V_m\ (eV)$	-3.38732	-16.26957	-10.53337
$E(AO/HO)\ (eV)$	-15.56407	-15.56407	-15.56407
$\Delta E_{H_2MO}(AO/HO)\ (eV)$	0	0	0
$E_T(AO/HO)\ (eV)$	-15.56407	-15.56407	-15.56407
$E_T(H_2MO)\ (eV)$	-31.63537	-67.69451	-49.66493
$E_T(atom-atom, msp^3.AO)\ (eV)$	-1.85836	0	0
$E_T(MO)\ (eV)$	-33.49373	-67.69450	-49.66493
$\omega\ (10^{15}\ rad/s)$	9.43699	24.9286	24.2751
$E_K\ (eV)$	6.21159	16.40846	15.97831
$\bar{E}_D\ (eV)$	-0.16515	-0.25352	-0.25017
$\bar{E}_{Kvib}\ (eV)$	0.12312 [2]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))
$\bar{E}_{osc}\ (eV)$	-0.10359	-0.22757	-0.14502
$E_{mag}\ (eV)$	0.14803	0.14803	0.14803
$E_T(Group)\ (eV)$	-33.59732	-67.92207	-49.80996
$E_{initial}(c_4\ AO/HO)\ (eV)$	-14.63489	-14.63489	-14.63489
$E_{initial}(c_5\ AO/HO)\ (eV)$	0	-13.59844	-13.59844
$E_D(Group)\ (eV)$	4.32754	12.49186	7.83016

Table 15.7. The total bond energies of n-alkanes calculated using the functional group composition and the energies of Table 15.6 compared to the experimental values [3].

Formula	Name	$C-C$	CH_3	CH_2	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_3H_8	Propane	2	2	1	41.46896	41.434	-0.00085
C_4H_{10}	Butane	3	2	2	53.62666	53.61	-0.00036
C_5H_{12}	Pentane	4	2	3	65.78436	65.77	-0.00017
C_6H_{14}	Hexane	5	2	4	77.94206	77.93	-0.00019
C_7H_{16}	Heptane	6	2	5	90.09976	90.09	-0.00013
C_8H_{18}	Octane	7	2	6	102.25746	102.25	-0.00006
C_9H_{20}	Nonane	8	2	7	114.41516	114.40	-0.00012
$C_{10}H_{22}$	Decane	9	2	8	126.57286	126.57	-0.00003
$C_{11}H_{24}$	Undecane	10	2	9	138.73056	138.736	0.00004
$C_{12}H_{26}$	Dodecane	11	2	10	150.88826	150.88	-0.00008
$C_{18}H_{38}$	Octadecane	18	2	16	223.83446	223.85	0.00008

Table 15.8. The bond angle parameters of straight-chain alkanes and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom, msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493 C_a	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493 C_a	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	

BRANCHED ALKANES (C_nH_{2n+2}, $n = 3,4,5...\infty$)

The branched-chain alkanes, C_nH_{2n+2}, comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-alkane groups are solved using the same principles as those used to solve the methyl and methylene functional groups wherein the $2s$ and $2p$ AOs of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. $E_T\left(atom-atom, msp^3.AO\right)$ of each $C-C$-bond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is $-1.85836\ eV$ or $-1.44915\ eV$ based on the energy match between the $C2sp^3$ HOs corresponding to the energy contributions equivalent to those of methylene, $-0.92918\ eV$ (Eq. (14.513), or methyl, $-0.72457\ eV$ (Eq. (14.151)), groups, respectively.

The symbols of the functional groups of branched-chain alkanes are given in Table 15.9. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkanes are given in Tables 15.10, 15.11, and 15.12, respectively. The total energy of each branched-chain alkane given in Table 15.13 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.12 corresponding to functional-group composition of the molecule. The bond angle parameters of branched-chain alkanes determined using Eqs. (15.79-15.108) are given in Table 15.14.

Table 15.9. The symbols of functional groups of branched alkanes.

Functional Group	Group Symbol
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.10. The geometrical bond parameters of branched alkanes and experimental values [1].

Parameter	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (\AA)$	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(\AA)$	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.11. The MO to HO intercept geometrical bond parameters of branched-chain alkanes. R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C-H\ (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\ (CH)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ ($C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ ($C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.12. The energy parameters (eV) of functional groups of branched-chain alkanes.

Parameters	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	3	2	1	1	1	1	1	1	1
n_2	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0
C_1	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1
c_2	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	1	1	0	0	0	1	1	0
c_4	1	1	1	2	2	2	2	2	2
c_5	3	2	1	0	0	0	0	0	0
C_{1o}	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	1	1	1	1	1	1	1	1	1
$V_e\ (eV)$	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_p\ (eV)$	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
$T\ (eV)$	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$V_m\ (eV)$	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(_{AO/HO})\ (eV)$	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(_{AO/HO})\ (eV)$	0	0	0	0	0	0	0	0	0
$E_T(_{AO/HO})\ (eV)$	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(_{H_2MO})\ (eV)$	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T\left(atom-atom,msp^3.AO\right)\ (eV)$	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(_{MO})\ (eV)$	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\ \left(10^{15}\ rad/s\right)$	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_K\ (eV)$	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D\ (eV)$	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}\ (eV)$	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}\ (eV)$	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{mag}\ (eV)$	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(_{Group})\ (eV)$	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(_{c_4\ AO/HO})\ (eV)$	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(_{c_5\ AO/HO})\ (eV)$	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(_{Group})\ (eV)$	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.13. The total bond energies of branched alkanes calculated using the functional group composition and the energies of Table 15.12 compared to the experimental values [3].

Formula	Name	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_4H_{10}	Isobutane	3	0	1	0	3	0	0	0	0	53.69922	53.695	-0.00007
C_5H_{12}	Isopentane	3	1	1	1	3	0	0	0	0	65.85692	65.843	-0.00021
C_5H_{12}	Neopentane	4	0	0	0	0	4	0	0	0	65.86336	65.992	0.00195
C_6H_{14}	2-Methylpentane	3	2	1	2	3	0	0	0	0	78.01462	78.007	-0.00010
C_6H_{14}	3-Methylpentane	3	2	1	2	3	0	0	0	0	78.01462	77.979	-0.00046
C_6H_{14}	2,2-Dimethylbutane	4	1	0	1	0	4	0	0	0	78.02106	78.124	0.00132
C_6H_{14}	2,3-Dimethylbutane	4	0	2	0	4	0	1	0	0	77.99581	78.043	0.00061
C_7H_{16}	2-Methylhexane	3	3	1	3	3	0	0	0	0	90.17232	90.160	-0.00014
C_7H_{16}	3-Methylhexane	3	3	1	3	3	0	0	0	0	90.17232	90.127	-0.00051
C_7H_{16}	3-Ethylpentane	3	3	1	3	3	0	0	0	0	90.17232	90.108	-0.00072
C_7H_{16}	2,2-Dimethylpentane	4	2	0	2	0	4	0	0	0	90.17876	90.276	0.00107
C_7H_{16}	2,2,3-Trimethylbutane	5	0	1	0	2	3	0	0	1	90.22301	90.262	0.00044
C_7H_{16}	2,4-Dimethylpentane	4	1	2	0	6	0	0	0	0	90.24488	90.233	-0.00013
C_7H_{16}	3,3-Dimethylpentane	4	2	0	2	0	4	0	0	0	90.17876	90.227	0.00054
C_8H_{18}	2-Methylheptane	3	4	1	4	3	0	0	0	0	102.33002	102.322	-0.00008
C_8H_{18}	3-Methylheptane	3	4	1	4	3	0	0	0	0	102.33002	102.293	-0.00036
C_8H_{18}	4-Methylheptane	3	4	1	4	3	0	0	0	0	102.33002	102.286	-0.00043
C_8H_{18}	3-Ethylhexane	3	4	1	3	4	0	0	0	0	102.30169	102.274	-0.00027
C_8H_{18}	2,2-Dimethylhexane	4	3	0	3	0	4	0	0	0	102.33646	102.417	0.00079
C_8H_{18}	2,3-Dimethylhexane	4	2	2	2	4	0	1	0	0	102.31121	102.306	-0.00005
C_8H_{18}	2,4-Dimethylhexane	4	2	2	1	6	0	0	0	0	102.40258	102.362	-0.00040
C_8H_{18}	2,5-Dimethylhexane	4	2	2	1	6	0	0	0	0	102.40258	102.396	-0.00006
C_8H_{18}	3,3-Dimethylhexane	4	3	0	3	0	4	0	0	0	102.33646	102.369	0.00032
C_8H_{18}	3,4-Dimethylhexane	4	2	2	2	4	0	1	0	0	102.31121	102.296	-0.00015
C_8H_{18}	3-Ethyl-2-methylpentane	4	2	2	2	4	0	1	0	0	102.31121	102.277	-0.00033
C_8H_{18}	3-Ethyl-3-methylpentane	4	3	0	3	0	4	0	0	0	102.33646	102.317	-0.00019
C_8H_{18}	2,2,3-Trimethylpentane	5	1	1	1	2	3	0	0	1	102.38071	102.370	-0.00010
C_8H_{18}	2,2,4-Trimethylpentane	5	1	1	0	3	4	0	0	0	102.40902	102.412	0.00003
C_8H_{18}	2,3,3-Trimethylpentane	5	1	1	1	2	3	0	0	1	102.38071	102.332	-0.00048
C_8H_{18}	2,3,4-Trimethylpentane	5	0	3	0	5	0	2	0	0	102.29240	102.342	0.00049
C_8H_{18}	2,2,3,3-Tetramethylbutane	6	0	0	0	0	6	0	1	0	102.41632	102.433	0.00016
C_9H_{20}	2,3,5-Trimethylhexane	5	1	3	0	7	0	1	0	0	114.54147	114.551	0.00008
C_9H_{20}	3,3-Diethylpentane	4	4	0	4	0	4	0	0	0	114.49416	114.455	-0.00034
C_9H_{20}	2,2,3,3-Tetramethylpentane	6	1	0	1	0	6	0	1	0	114.57402	114.494	-0.00070
C_9H_{20}	2,2,3,4-Tetramethylpentane	6	0	2	0	3	3	1	0	1	114.51960	114.492	-0.00024
C_9H_{20}	2,2,4,4-Tetramethylpentane	6	1	0	0	0	8	0	0	0	114.57316	114.541	-0.00028
C_9H_{20}	2,3,3,4-Tetramethylpentane	6	0	2	0	4	2	0	0	2	114.58266	114.484	-0.00086
$C_{10}H_{22}$	2-Methylnonane	3	6	1	6	3	0	0	0	0	126.64542	126.680	0.00027
$C_{10}H_{22}$	5-Methylnonane	3	6	1	6	3	0	0	0	0	126.64542	126.663	0.00014

Table 15.14. The bond angle parameters of branched-chain alkanes and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom, msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

ALKENES (C_nH_{2n}, $n = 3,4,5...\infty$)

The straight and branched-chain alkenes, C_nH_{2n}, comprise at least one carbon-carbon double bond comprising a functional group that is solved equivalently to the double bond of ethylene. The double bond may be bound to one, two, three, or four carbon single bonds that substitute for the hydrogen atoms of ethylene. Based on the condition of energy matching of the orbital, any magnetic energy due to unpaired electrons in the constituent fragments, and differences in oscillation in the transition state, three distinct functional groups can be identified: C vinyl single bond to $-C(C)=C$, C vinyl single bond to $-C(H)=C$, and C vinyl single bond to $-C(C)=CH_2$. In addition, CH_2 of the $-C=CH_2$ moiety is an alkene functional group.

The alkyl portion of the alkene may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in alkenes are equivalent to those in branched-chain alkanes. The solution of the functional groups comprises the hybridization of the $2s$ and $2p$ AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. $E_T\left(atom-atom,msp^3.AO\right)$ of the $C=C$-bond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is equivalent to that of ethylene, $-2.26759\ eV$, given by Eq. (14.247). $E_T\left(atom-atom,msp^3.AO\right)$ of each $C-C$-bond MO in Eq. (15.52) is $-1.85836\ eV$ or $-1.44915\ eV$ based on the energy match between the $C2sp^3$ HOs corresponding to the energy contributions equivalent to those of methylene, $-0.92918\ eV$ (Eq. (14.513), or methyl, $-0.72457\ eV$ (Eq. (14.151)), groups, respectively.

The symbols of the functional groups of alkenes are given in Table 15.15. The geometrical (Eqs. (15.1-15.5) and (15.41)), intercept (Eqs. (15.71-15.78)), and energy (Eqs.

(15.6-15.11) and (15.17-15.56)) parameters of alkenes are given in Tables 15.16, 15.17, and 15.18, respectively. The total energy of each alkene given in Table 15.19 was calculated as the sum over the integer multiple of each $E_D(_{Group})$ of Table 15.18 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage , the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(_{Group})$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of alkenes determined using Eqs. (15.79-15.108) are given in Table 15.20.

Table 15.15. The symbols of functional groups of alkenes.

Functional Group	Group Symbol
CC double bond	$C=C$
C vinyl single bond to -C(C)=C	$C-C$ (i)
C vinyl single bond to -C(H)=C	$C-C$ (ii)
C vinyl single bond to -C(C))=CH$_2$	$C-C$ (iii)
CH$_2$ alkenyl group	$C-H\ (CH_2)$ (i)
CH$_3$ group	$C-H\ (CH_3)$
CH$_2$ alkyl group	$C-H\ (CH_2)$ (ii)
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.16. The geometrical bond parameters of alkenes and experimental values [1].

Parameter	$C=C$ Group	$C-C$ (i) Group	$C-C$ (ii) Group	$C-C$ (iii) Group	$C-H\ (CH_2)$ (i) Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ (ii) Group	$C-H$ Group
$a\ (a_0)$	1.47228	2.04740	2.04740	2.04740	1.64010	1.64920	1.67122	1.67465
$c'\ (a_0)$	1.26661	1.43087	1.43087	1.43087	1.04566	1.04856	1.05553	1.05661
Bond Length $2c'$ (Å)	1.34052	1.51437	1.51437	1.51437	1.10668	1.10974	1.11713	1.11827
Exp. Bond Length (Å)	1.342 (2-methylpropene) 1.346 (2-butene) 1.349 (1,3-butadiene)		1.508 (2-butene)	1.508 (2-methylpropene)	1.10 (2-methylpropene) 1.108 (avg.) (1,3-butadiene)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)
$b,c\ (a_0)$	0.75055	1.46439	1.46439	1.46439	1.26354	1.27295	1.29569	1.29924
e	0.86030	0.69887	0.69887	0.69887	0.63756	0.63580	0.63159	0.63095

Parameter	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ (Å)	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.17. The MO to HO intercept geometrical bond parameters of alkenes. R_1 is an alkyl group and R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C_c(H)C_a=C_a(H)C_d$	C_a	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	127.61	52.39	58.24	0.77492	0.49168
$C_c(H)C_a=C_bH_2$	C_b	-1.13380	0	0	0	-152.74949	0.91771	0.85252	-15.95955	-15.76868	129.84	50.16	60.70	0.72040	0.54620
$C_c(C_d)C_a=C_bH_2C_e$	C_a	-1.13380	-0.72457	-0.72457	0	-154.19863	0.91771	0.78155	-17.40869	-17.21783	126.39	53.61	56.95	0.80289	0.46371
$R_1C_bH_2-C_a(C)=C$ $(C-C\ \text{(i)})$	C_a	-1.13380	-0.72457	-0.72457	0	-154.19863	0.91771	0.78155	-17.40869	-17.21783	60.88	119.12	27.79	1.81127	0.38039
$R_1C_bH_2-C_a(C)=C$ $(C-C\ \text{(i)})$ $R_1C_bH_2-C_a(C)=CH_2$ $(C-C\ \text{(iii)})$	C_b	-0.72457	-0.92918	0	0	-153.26945	0.91771	0.82562	-16.47951	-16.28864	67.40	112.60	31.36	1.74821	0.31734
$R_1C_bH_2-C_a(H)=C$ $(C-C\ \text{(ii)})$	C_a	-1.13380	-0.92918	0	0	-153.67866	0.91771	0.80561	-16.88873	-16.69786	64.57	115.43	29.79	1.77684	0.34596
$R_1C_bH_2-C_a(H)=C$ $(C-C\ \text{(i)})$	C_b	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	65.99	114.01	30.58	1.76270	0.33183
$C-H\ (CH_2)$ (i)	C	-1.13380	0	0	0	-152.74949	0.91771	0.85252	-15.95955	-15.76868	77.15	102.85	41.13	1.23531	0.18965
$C-H\ (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$ (ii)	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\ (CH)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ $(C-C\ \text{(a)})$	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ $(C-C\ \text{(a)})$	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b(H_2C_c-R')HCH_2-$ $(C-C\ \text{(b)})$	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C\ \text{(c)})$	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b(H_2C_c-R')HCH_2-$ $(C-C\ \text{(d)})$	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C\ \text{(e)})$	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b(H_2C_c-R')HCH_2-$ $(C-C\ \text{(f)})$	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C\ \text{(f)})$	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.18. The energy parameters (eV) of functional groups of alkenes.

Parameters	$C=C$ Group	$C-C$ (i) Group	$C-C$ (ii) Group	$C-C$ (iii) Group	CH_2 (i) Group	CH_3 Group	CH_2 (ii) Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	2	1	1	1	2	3	2	1	1	1	1	1	1	1
n_2	0	0	0	0	1	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	0.91771	1	1	1	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
c_2	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	1	0	1	1	0	1	1	0	0	0	1	1	0
c_4	4	2	2	2	1	1	1	1	2	2	2	2	2	2
c_5	0	0	0	0	2	3	2	1	0	0	0	0	0	0
C_{1o}	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	0.91771	1	1	1	1	1	1	1	1	1	1	1	1	1
$V_e\ (eV)$	-102.08992	-30.19634	-30.19634	-30.19634	-72.03287	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_p\ (eV)$	21.48386	9.50874	9.50874	9.50874	26.02344	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
$T\ (eV)$	34.67062	7.37432	7.37432	7.37432	21.95990	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$V_m\ (eV)$	-17.33531	-3.68716	-3.68716	-3.68716	-10.97995	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(AO/HO)\ (eV)$	0	-14.63489	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(AO/HO)\ (eV)$	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$E_T(AO/HO)\ (eV)$	0	-14.63489	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(H_2MO)\ (eV)$	-63.27075	-31.63534	-31.63534	-31.63534	-49.66437	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom, msp^3.AO)\ (eV)$	-2.26759	-1.44915	-1.85836	-1.44915	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(MO)\ (eV)$	-65.53833	-33.08452	-33.49373	-33.08452	-49.66493	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\ (10^{15}\ rad/s)$	43.0680	9.97851	16.4962	9.97851	25.2077	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_K\ (eV)$	28.34813	6.56803	10.85807	6.56803	16.59214	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D\ (eV)$	-0.34517	-0.16774	-0.21834	-0.16774	-0.25493	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}\ (eV)$	0.17897 [6]	0.15895 [7]	0.09931 [8]	0.09931 [8]	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}\ (eV)$	-0.25568	-0.08827	-0.16869	-0.11809	-0.07727	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{mag}\ (eV)$	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(Group)\ (eV)$	-66.04969	-33.17279	-33.66242	-33.20260	-49.81948	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(c_4\ AO/HO)\ (eV)$	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(c_5\ AO/HO)\ (eV)$	0	0	0	0	-13.59844	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(Group)\ (eV)$	7.51014	3.75498	4.39264	3.78480	7.83968	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.19. The total bond energies of alkenes calculated using the functional group composition and the energies of Table 15.18 compared to the experimental values [2]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(_{Group})$ (eV) values based on composition is given by (15.58).

Formula	Name	$C=C$	$C-C$ (i)	$C-C$ (ii)	$C-C$ (iii)	CH_2 (i)	CH_3	CH_2 (ii)	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_3H_6	Propene	0	0	1	0	1	1	0	1	0	0	0	0	0	0	0	35.56033	35.63207	0.00201
C_4H_8	1-Butene	1	0	0	0	1	1	1	1	1	0	0	0	0	0	0	47.71803	47.78477	0.00140
C_4H_8	trans-2-Butene	1	0	2	0	0	2	0	2	0	0	0	0	0	0	0	47.93116	47.90395	-0.00057
C_4H_8	Isobutene	1	0	0	2	1	2	0	0	0	0	0	0	0	0	0	47.90314	47.96096	0.00121
C_5H_{10}	1-Pentene	1	0	1	0	1	1	2	1	1	0	0	0	0	0	0	59.87573	59.95094	0.00125
C_5H_{10}	trans-2-Pentene	1	0	2	0	0	2	1	2	1	0	0	0	0	0	0	60.08886	60.06287	-0.00043
C_5H_{10}	2-Methyl-1-butene	1	0	0	2	1	2	1	0	1	0	0	0	0	0	0	60.06084	60.09707	0.00060
C_5H_{10}	2-Methyl-2-butene	1	1	1	0	0	3	0	1	0	0	0	0	0	0	0	60.21433	60.16444	-0.00083
C_5H_{10}	3-Methyl-1-butene	1	0	1	0	1	3	0	2	0	2	0	0	0	0	0	59.97662	60.01727	0.00068
C_6H_{12}	1-Hexene	1	0	1	0	1	1	3	1	3	0	0	0	0	0	0	72.03343	72.12954	0.00133
C_6H_{12}	trans-2-Hexene	1	0	2	0	0	2	2	2	2	0	0	0	0	0	0	72.24656	72.23733	-0.00013
C_6H_{12}	trans-3-Hexene	1	0	2	0	0	2	2	2	2	0	0	0	0	0	0	72.24656	72.24251	-0.00006
C_6H_{12}	2-Methyl-1-pentene	1	0	0	2	1	2	2	0	2	0	0	0	0	0	0	72.21854	72.29433	0.00105
C_6H_{12}	2-Methyl-2-pentene	1	2	1	0	0	3	1	1	1	0	0	0	0	0	0	72.37203	72.37206	0.00000
C_6H_{12}	3-Methyl-1-pentene	1	0	1	0	1	2	1	2	1	2	0	0	0	0	0	72.13432	72.19173	0.00080
C_6H_{12}	4-Methyl-1-pentene	1	0	1	0	1	2	1	2	0	3	0	0	0	0	0	72.10599	72.21038	0.00145
C_6H_{12}	3-Methyl-trans-2-pentene	1	2	1	0	0	3	1	1	1	0	0	0	0	0	0	72.37203	72.33268	-0.00054
C_6H_{12}	4-Methyl-trans-2-pentene	1	0	2	0	0	3	0	3	0	2	0	0	0	0	0	72.34745	72.31610	-0.00043
C_6H_{12}	2-Ethyl-1-butene	1	0	0	2	1	2	2	0	4	0	0	0	0	0	0	72.21854	72.25909	0.00056
C_6H_{12}	2,3-Dimethyl-1-butene	1	0	0	2	1	3	0	1	0	2	0	0	0	0	0	72.31943	72.32543	0.00008
C_6H_{12}	3,3-Dimethyl-1-butene	1	0	1	0	1	3	0	1	0	0	3	0	0	0	-1	72.31796	72.30366	-0.00020
C_6H_{12}	2,3-Dimethyl-2-butene	1	4	0	0	0	4	0	0	0	0	0	0	0	0	0	72.49750	72.38450	-0.00156
C_7H_{14}	1-Heptene	1	0	1	0	1	1	4	1	4	0	0	0	0	0	0	84.19113	84.27084	0.00095
C_7H_{14}	5-Methyl-1-hexene	1	0	1	0	1	2	2	2	1	3	0	0	0	0	0	84.26369	84.30608	0.00050
C_7H_{14}	trans-3-Methyl-3-hexene	1	2	1	0	0	3	2	1	2	0	0	0	0	0	0	84.52973	84.42112	-0.00129
C_7H_{14}	2,4-Dimethyl-1-pentene	1	0	0	2	1	3	1	1	0	3	0	0	0	0	0	84.44880	84.49367	0.00053
C_7H_{14}	4,4-Dimethyl-1-pentene	1	0	1	0	1	3	1	1	0	0	4	0	0	0	0	84.27012	84.47087	0.00238
C_7H_{14}	2,4-Dimethyl-2-pentene	1	2	1	0	0	4	0	2	0	2	0	0	0	0	0	84.63062	84.54445	-0.00102
C_7H_{14}	trans-4,4-Dimethyl-2-pentene	1	0	2	0	0	4	0	2	0	0	3	0	0	0	-2	84.54076	84.54549	0.00006
C_7H_{14}	2-Ethyl-3-methyl-1-butene	1	0	0	2	1	3	1	1	1	2	0	0	0	0	0	84.47713	84.44910	-0.00033
C_7H_{14}	2,3,3-Trimethyl-1-butene	1	0	0	2	1	4	0	0	0	0	3	0	0	0	-2	84.51274	84.51129	-0.00002
C_8H_{16}	1-Octene	1	0	0	1	1	1	5	1	5	0	0	0	0	0	0	96.34883	96.41421	0.00068
C_8H_{16}	trans-2,2-Dimethyl-3-hexene	1	0	2	0	0	4	1	2	1	0	3	0	0	0	-2	96.69846	96.68782	-0.00011
C_8H_{16}	3-Ethyl-2-methyl-1-pentene	1	0	0	2	1	3	2	1	2	2	0	0	0	0	0	96.63483	96.61113	-0.00025
C_8H_{16}	2,4,4-Trimethyl-1-pentene	1	0	0	2	1	4	1	0	0	0	4	0	0	0	0	96.61293	96.71684	0.00107
C_8H_{16}	2,4,4-Trimethyl-2-pentene	0	2	1	0	0	5	0	1	0	0	3	0	0	0	-3	96.67590	96.65880	-0.00018
$C_{10}H_{20}$	1-Decene	1	0	1	0	1	1	7	1	7	0	0	0	0	0	0	120.66423	120.74240	0.00065
$C_{12}H_{24}$	1-Dodecene	1	0	1	0	1	1	9	1	9	0	9	0	0	0	0	144.97963	145.07163	0.00063
$C_{16}H_{32}$	1-Hexadecene	1	0	1	0	1	1	13	1	13	0	0	0	0	0	0	193.61043	193.71766	0.00055

Table 15.20. The bond angle parameters of alkenes and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HC_aC_c$ $(C_c(H)C_a=C_b)$	2.11323	2.86175	4.2895	-15.95954 C_a	9	-14.82575 C_c	1	0.85252	0.91771	0.75	1	0.75	1.07647	0				118.36	
$\angle C_cC_aC_c$ $(C_c(C_c)C_a=C_b)$	2.86175	2.86175	4.7958	-16.68411 C_c	24	-16.68411 C_c	24	0.81549	0.81549	1	1	1	0.81549	-1.85836				113.84	
$\angle C_bC_aC_c$ $(C_b=C_aC_c)$	2.53321	2.86175	4.7539	-16.88873 C_b	27	-16.68411 C_c	24	0.80561	0.81549	1	1	1	0.81055	-1.85836				123.46	124.4 (1,3,5-hexatriene CbCcCc) 121.7 (1,3,5-hexatriene CaCbCc) 124.4 (1,3-butadiene CCC) 125.3 (2-butene CbCaCc)
$\angle HC_aC_b$																118.36	123.46	118.19	
$\angle HC_aH$ $(H_2C_a=C_bC_c)$	2.04578	2.04578	3.4756	-15.95955	9	H	H	0.85252	1	1	1	0.75	1.17300	0				116.31	118.5 (2-methylpropene)
$\angle C_bC_aH$ $(H_2C_a=C_bC_c)$																116.31		121.85	121 (2-methylpropene)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

ALKYNES (C_nH_{2n-2}, $n = 3,4,5...\infty$)

The straight and branched-chain alkynes, C_nH_{2n-2}, have at least one carbon-carbon triple bond comprising a functional group that is solved equivalently to the triple bond of acetylene. The triple bond may be bound to one or two carbon single bonds that substitute for the hydrogen atoms of acetylene. Based on the energy matching of the mutually bound C, these $C-C$-bond MOs are defined as primary and secondary $C-C$ functional groups, respectively, that are unique to alkynes. In addition, the corresponding terminal CH of a primary alkyne comprises a functional group that is solved equivalently to the methylyne group of acetylene as given in the Acetylene Molecule section.

The alkyl portion of the alkyne may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in alkynes are equivalent to those in branched-chain alkanes.

The solution of the functional groups comprises the hybridization of the $2s$ and $2p$ AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. $E_T(atom-atom,msp^3.AO)$ of the $C \equiv C$-bond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is equivalent to that of acetylene, $-3.13026\ eV$, given by Eq. (14.342). $E_T(atom-atom,msp^3.AO)$ of each -alkyl-bond MO in Eq. (15.52) is $-1.85836\ eV$ or $-1.44915\ eV$ based on the energy match between the $C2sp^3$ HOs corresponding to the energy contributions equivalent to those of methylene, $-0.92918\ eV$ (Eq. (14.513), or methyl, $-0.72457\ eV$ (Eq. (14.151)), groups, respectively. For the $C-C$ groups each comprising a C single bond to $C \equiv C$, $E_T(atom-atom,msp^3.AO)$ is $-0.72457\ eV$ based on the energy match between the $C2sp^3$ HOs for the mutually bound C of the single and triple bonds. The parameter ω of each group is matched for oscillation in the transition state based on the group being primary or secondary.

The symbols of the functional groups of alkynes are given in Table 15.21. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkynes are given in Tables 15.22, 15.23, and 15.24, respectively. The total energy of each alkyne given in Table 15.25 is calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.24 corresponding to functional-group composition of the molecule. The bond angle parameters of alkynes determined using Eqs. (15.79-15.108) are given in Table 15.26. Each C of the $C \equiv C$ group can further bond with only one atom, and the bond is linear as a minimum of energy as in the case of acetylene.

Table 15.21. The symbols of functional groups of alkynes.

Functional Group	Group Symbol
CC triple bond	$C \equiv C$
C single bond to $C \equiv C$ (1°)	$C-C$ (i)
C single bond to $C \equiv C$ (2°)	$C-C$ (ii)
CH (terminal)	$C-H$ (i)
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH (alkyl)	$C-H$ (ii)
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.22. The geometrical bond parameters of alkynes and experimental values [1].

Parameter	$C \equiv C$ Group	$C-C$ (i) Group	$C-C$ (ii) Group	$C-H$ (i) Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ (ii) Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.28714	1.99185	1.99185	1.48719	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.13452	1.41133	1.41133	0.99572	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ (Å)	1.20072	1.49369	1.49369	1.05383	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.203 (acetylene) 1.208 (2,4-hexadiyne)	1.450 (2,4-hexadiyne)	1.450 (2,4-hexadiyne)	1.060 (acetylene)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	0.60793	1.40557	1.40557	1.10466	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.88143	0.70855	0.70855	0.66953	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.23. The MO to HO intercept geometrical bond parameters of alkynes. E_T is $E_T(atom-atom, msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$RC_cC_bC_a-H$	C_a	-1.56513	0	0	0	-153.18082	0.91771	0.83008	-16.39088	-16.20002	90.99	89.01	48.71	0.98144	0.01428
$C_cC_a\equiv C_bH$	C_a	-1.56513	-0.36229	0	0	-153.54311	0.91771	0.81213	-16.75317	-16.56231	137.17	42.83	65.25	0.53890	0.59562
$C_cC_a\equiv C_bH$	C_b	-1.56513	0	0	0	-153.18082	0.91771	0.83008	-16.39088	-16.20002	137.91	42.09	66.24	0.51853	0.61599
$C_c-C_a\equiv C_bH$	C_c	-0.36229	-0.92918	0	0	-152.90716	0.91771	0.84418	-16.11722	-15.92636	75.71	104.29	35.59	1.61974	0.20841
$C-H\ (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\ (CH)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ $(C-C\ \text{(a)})$	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ $(C-C\ \text{(a)})$	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b(H_2C_c-R')HCH_2-$ $(C-C\ \text{(b)})$	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C\ \text{(c)})$	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b(H_2C_c-R')HCH_2-$ $(C-C\ \text{(d)})$	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C\ \text{(e)})$	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b(H_2C_c-R')HCH_2-$ $(C-C\ \text{(f)})$	C_b	-0.72457	-0.92918	-0.92918	0	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C\ \text{(f)})$	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.24. The energy parameters (eV) of functional groups of alkynes.

Parameters	$C\equiv C$ Group	$C-C$ (i) Group	$C-C$ (ii) Group	$C-H$ (i) Group	CH_3 Group	CH_2 Group	$C-H$ (ii) Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	3	1	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1	1	1
c_2	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	2	1	1	0	0	1	1	0	0	0	1	1	0
c_4	6	2	2	1	1	1	1	2	2	2	2	2	2
c_5	0	0	0	1	3	2	1	0	0	0	0	0	0
C_{1o}	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	1	1	1	1	1	1	1	1	1	1	1	1	1
V_e (eV)	-182.53826	-31.29307	-31.29307	-40.62396	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	35.97770	9.64042	9.64042	13.66428	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	70.90876	7.85528	7.85528	13.65796	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_m (eV)	-35.45438	-3.92764	-3.92764	-6.82898	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(_{AO/HO})$ (eV)	-16.20002	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(_{AO/HO})$ (eV)	0	-0.72457	-0.72457	-3.130269	0	0	0	0	0	0	0	0	0
$E_T(_{AO/HO})$ (eV)	-16.20002	-13.91032	-13.91032	-11.50462	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(_{H_2MO})$ (eV)	-94.90616	-31.63533	-31.63533	-31.63532	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T\left(atom-atom,msp^3.AO\right)$ (eV)	-3.13026	-0.72457	-0.72457	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(_{MO})$ (eV)	-98.03637	-32.35994	-32.35994	-31.63537	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω $\left(10^{15}\ rad/s\right)$	20.0186	10.3988	17.5426	30.8370	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	13.17659	6.84470	11.54682	20.29747	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D$ (eV)	-0.23468	-0.16749	-0.21754	-0.28197	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}$ (eV)	0.27773 [9]	0.08989 [9]	0.08989 [9]	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}$ (eV)	-0.09581	-0.12255	-0.17260	-0.10430	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mag} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(_{Group})$ (eV)	-98.02775	-32.48249	-32.53254	-31.73967	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(_{c_4\ AO/HO})$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(_{c_5\ AO/HO})$ (eV)	0	0	0	-13.59844	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(_{Group})$ (eV)	10.21841	3.21271	3.26276	3.50634	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.25. The total bond energies of alkynes calculated using the functional group composition and the energies of Table 15.24 compared to the experimental values [2].

Formula	Name	$C\equiv C$	$C-C$ (i)	$C-C$ (ii)	CH (i)	CH_3	CH_2	CH (ii)	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_3H_4	Propyne	1	1	0	1	1	0	0	0	0	0	0	0	0	29.42932	29.40432	-0.00085
C_4H_6	1-Butyne	1	1	0	1	1	1	0	1	0	0	0	0	0	41.58702	41.55495	-0.00077
C_4H_6	2-Butyne	1	0	2	0	2	0	0	0	0	0	0	0	0	41.72765	41.75705	0.00070
C_9H_{16}	1-Nonyne	1	1	0	1	1	6	0	6	0	0	0	0	0	102.37552	102.35367	-0.00021

Table 15.26. The bond angle parameters of alkynes and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom, msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle C_cC_aC_b$ $(C_cC_a\equiv C_bH)$																		180	
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

ALKYL FLUORIDES ($C_nH_{2n+2-m}F_m$, $n=1,2,3,4,5...\infty$ $m=1,2,3...\infty$)

The branched-chain alkyl fluorides, $C_nH_{2n+2-m}F_m$, may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds wherein at least one H is replaced by a fluorine. The $C-F$ bond comprises a functional group for each case of F replacing a H of methane in the series $H_{4-m}C-F_m$, $m=1,2,3,4$, and F replacing a H of an alkane. The methyl, methylene, methylyne functional groups are equivalent to those of branched-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the $C-F$ functional groups comprises the hybridization of the $2s$ and $2p$ AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the F AO to form a molecular orbital (MO) permits each participating orbital to decrease in radius and energy. In alkyl fluorides, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3)=-14.63489\ eV$ (Eq. (15.25)), and the F AO has an energy of $E(F)=-17.42282\ eV$. To meet the equipotential condition of the union of the $C-F$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the $C-F$-bond MO given by Eqs. (15.68) and (15.70) is

$$c_2(C2sp^3HO\ to\ F)=\frac{E(C,2sp^3)}{E(F)}c_2(C2sp^3HO)=\frac{-14.63489\ eV}{-17.42282\ eV}(0.91771)=0.77087 \quad (15.110)$$

$E_T(atom-atom,msp^3.AO)$ of the $C-F$-bond MO in Eq. (15.52) based on the charge donation from F to the MO is determined by the linear combination that results in a energy that is a minimum which does not exceed the energy of the AO of the F atom to which it is energy matched.

The symbols of the functional groups of branched-chain alkyl fluorides are given in Table 15.27. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkyl fluorides are

given in Tables 15.28, 15.29, and 15.30, respectively. The total energy of each branched-chain alkyl fluoride given in Table 15.31 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.30 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). In the case of trifluoromethane, E_{mag} is positive since the term due to the fluorine atoms cancels that of the CH group. The $C-C$ bonds to the CHF group (one H bond to C) were each treated as an iso $C-C$ bond. The $C-C$ bonds to the CF group (no H bonds to C) were each treated as a tert-butyl $C-C$. E_{mag} was subtracted for each t-butyl group. The bond angle parameters of branched-chain alkyl fluorides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.110) are given in Table 15.32.

Table 15.27. The symbols of functional groups of branched-chain alkyl fluorides.

Functional Group	Group Symbol
CF of CF_mH_{4-m}	$C-F$ (i)
CF of $C_nH_{2n+2-m}F_m$	$C-F$ (ii)
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.28. The geometrical bond parameters of branched-chain alkyl fluorides and experimental values [1].

Parameter	$C-F$ (i) Group	$C-F$ (ii) Group	$C-H$ (CH_3) Group	$C-H$ (CH_2) Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
a (a_0)	1.72139	1.72139	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
c' (a_0)	1.31202	1.31202	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ ($\mathring{A}$)	1.38858	1.38858	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length ($\mathring{A}$)	1.382 (methyl fluoride)	1.382 (methyl fluoride)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
b,c (a_0)	1.11435	1.11435	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.76219	0.76219	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.29. The MO to HO intercept geometrical bond parameters of branched-chain alkyl fluorides. R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$H_{4-m}C_a-F_m$ (C_a-F (i))	C_a	-1.34946	0	0	0	-152.96515	0.91771	0.84115	-16.17521	-15.98435	100.77	79.23	47.86	1.15488	0.15714
$H_{4-m}C_a-F_m$ (C_a-F (i))	F	-1.34946	0	0	0		0.78069	0.84115	-16.17521		100.77	79.23	47.86	1.15488	0.15714
$-H_2C_bC_aF$ (C_a-F (ii))	C_a	-1.34946	-0.92918	0	0	-153.89433	0.91771	0.79546	-17.10440	-16.91353	97.02	82.98	45.11	1.21483	0.09718
$-H_2C_bC_aF$ (C_a-F (ii))	F	-1.34946	0	0	0		0.78069	0.84115	-16.17521		100.77	79.23	47.86	1.15488	0.15714
$C-H$ (CH_3)	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H$ (CH_2)	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H$ (CH)	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ ($C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ ($C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.30. The energy parameters (eV) of functional groups of branched-chain alkyl fluorides.

Parameters	$C-F$ (i) Group	$C-F$ (ii) Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1
c_2	0.77087	0.77087	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	0	1	1	0	0	0	1	1	0
c_4	2	2	1	1	1	2	2	2	2	2	2
c_5	0	0	3	2	1	0	0	0	0	0	0
C_{1o}	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	1	1	1	1	1	1	1	1	1	1	1
V_e (eV)	-32.02108	-32.02108	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	10.37015	10.37015	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	9.30097	9.30097	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_m (eV)	-4.65048	-4.65048	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(AO/HO)$ (eV)	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(AO/HO)$ (eV)	0	0	0	0	0	0	0	0	0	0	0
$E_T(AO/HO)$ (eV)	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(H_2MO)$ (eV)	-31.63534	-31.63534	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom, msp^3.AO)$ (eV)	-2.69892	-2.69892	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(MO)$ (eV)	-34.33429	-34.33429	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω $(10^{15}\ rad/s)$	24.8506	12.9435	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	16.35707	8.51966	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D$ (eV)	-0.27472	-0.19826	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}$ (eV)	0.13849 [10]	0.10911 [11]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}$ (eV)	-0.20547	-0.14371	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mag} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(Group)$ (eV)	-34.53976	-34.47800	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(c_4\ AO/HO)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(c_5\ AO/HO)$ (eV)	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(Group)$ (eV)	5.26998	5.20822	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.31. The total bond energies of branched-chain alkyl fluorides calculated using the functional group composition and the energies of Table 15.30 compared to the experimental values [2]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by (15.58).

Formula	Name	$C-F$ (i)	$C-F$ (ii)	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CF_4	Tetrafluoromethane	4	0	0	0	0	0	0	0	0	0	0	0	21.07992	21.016	-0.00303
CHF_3	Trifluoromethane	3	0	0	0	1	0	0	0	0	0	0	1	19.28398	19.362	0.00405
CH_2F_2	Difluoromethane	2	0	0	1	0	0	0	0	0	0	0	0	18.37012	18.280	-0.00496
C_3H_7F	1-Fluoropropane	0	1	1	2	0	2	0	0	0	0	0	-1	41.86745	41.885	0.00041
C_3H_7F	2-Fluoropropane	0	1	2	0	1	0	2	0	0	0	0	-1	41.96834	41.963	-0.00012

Table 15.32. The bond angle parameters of branched-chain alkyl fluorides and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle FC_aF$ $(C_a-F$ (i))	2.62403	2.62403	4.3128	-16.17521 F	12	-16.17521 F	12	0.84115	0.84115	1	1	1	0.84115	-1.44915				110.53	108.8 (fluoroform)
$\angle HC_aF$ $(C_a-F$ (i))	2.11106	2.62403	3.8987	-17.10440 C_a	31	-17.42282 F	F	0.79546	0.78092 (Eq. (15.64))	0.75	1	0.75	0.98172	0				110.38	
$\angle C_bC_aF$ $(C_a-F$ (ii))	2.91547	2.62403	4.5826	-16.68412 C_b	25	-17.42282 F	F	0.81549	0.77087 (Eq. (15.110))	1	1	1	0.79318	-1.85836				111.53	110.3 (1,2-difluoroethane)
$\angle C_bC_aH$ $(C_a-F$ (ii))	2.91547	2.11106	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.83	111.0 (1,1-difluoroethane)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H		0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H		0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

ALKYL CHLORIDES ($C_nH_{2n+2-m}Cl_m$, $n=1,2,3,4,5...\infty$ $m=1,2,3...\infty$)

The branched-chain alkyl chlorides, $C_nH_{2n+2-m}Cl_m$, may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds wherein at least one H is replaced by a chlorine. The $C-Cl$ bond comprises a functional group for each case of Cl replacing a H of methane for the series $H_{4-m}C-Cl_m$, $m=1,2,3$, with the $C-Cl$ bond of CCl_4 comprising another functional group due to the limitation of the minimum energy of Cl matched to that of the $C2sp^3$ HO. In addition, the $C-Cl$ bond due to Cl replacing a H of an alkane is a function group. The methyl, methylene, methylyne functional groups are equivalent to those of branched-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the $C-Cl$ functional groups comprises the hybridization of the $2s$ and $2p$ AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the Cl AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl chlorides, the energy of chorine is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_2 in Eq. (15.52) is one, and the energy matching condition is determined by the C_2 parameter. Then, $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3)=-14.63489\ eV$ (Eq. (15.25)), and the Cl AO has an energy of $E(Cl)=-12.96764\ eV$. To meet the equipotential condition of the union of the $C-Cl$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor C_2 of Eq. (15.52) for the $C-Cl$-bond MO given by Eqs. (15.68) and (15.70) is

$$C_2(C2sp^3HO\ to\ Cl)=\frac{E(Cl)}{E(C,2sp^3)}c_2(C2sp^3HO)=\frac{-12.96764\ eV}{-14.63489\ eV}(0.91771)=0.81317 \quad (15.110)$$

The valence energy of the carbon $2p$ is $-11.2603\ eV$ and that of the Cl AO is $-12.96764\ eV$. The energy difference is more than that of $2E_T(C-C,2sp^3)$ given by Eq. (14.151) for a single

bond. Thus, $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-Cl$-bond MO in Eq. (15.52) due to the charge donation from the C and Cl atoms to the MO is $-1.44915\ eV$ based on the energy match between the $C2sp^3$ HO and the Cl AO corresponding to the energy contributions equivalent to those of methyl groups, $-0.72457\ eV$ (Eq. (14.151)).

The symbols of the functional groups of branched-chain alkyl chlorides are given in Table 15.33. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkyl chlorides are given in Tables 15.34, 15.35, and 15.36, respectively. The total energy of each branched-chain alkyl chloride given in Table 15.37 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.36 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that was subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The $C-C$ bonds to the $CHCl$ group (one H bond to C) were each treated as an iso $C-C$ bond. The $C-C$ bonds to the CCl group (no H bonds to C) were each treated as a tert-butyl $C-C$. E_{mag} was subtracted for each t-butyl group. The bond angle parameters of branched-chain alkyl chlorides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.111) are given in Table 15.38.

Table 15.33. The symbols of functional groups of branched-chain alkyl chlorides.

Functional Group	Group Symbol
CCl of CCl_mH_{4-m}	$C-Cl$ (i)
CCl of CCl_4	$C-Cl$ (ii)
CCl of $C_nH_{2n+2-m}Cl_m$	$C-Cl$ (iii)
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.34. The geometrical bond parameters of branched-chain alkyl chlorides and experimental values [1].

Parameter	$C-Cl$ (i) Group	$C-Cl$ (ii) Group	$C-Cl$ (iii) Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	2.32621	2.37026	2.32621	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.69136	1.70729	1.69136	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ (Å)	1.79005	1.80692	1.79005	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.785 (methyl chloride)	1.767 (carbon tetrachloride)	1.802 (ethyl chloride) 1.790 (1,2-dichloroethane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	1.59705	1.64416	1.59705	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.72709	0.72030	0.72709	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.35. The MO to HO intercept geometrical bond parameters of branched-chain alkyl chlorides. R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$H_{4-m}C_a-Cl_m$, $m=1,2,3$, (C_a-Cl (i))	C_a	-0.72457	0	0	0	-152.34026	0.91771	0.87495	-15.55033	-15.35946	69.62	110.38	30.90	1.99599	0.30463
$H_{4-m}C_a-Cl_m$, $m=1,2,3$, (C_a-Cl (i))	Cl	-0.72457	0	0	0		1.05158	0.87495	-15.55033		69.62	110.38	30.90	1.99599	0.30463
C_aCl_4 (C_a-Cl (ii))	C_a	-0.46459	0	0	0	-152.08028	0.91771	0.88983	-15.29034	-15.09948	66.98	113.02	29.87	2.05530	0.34801
C_aCl_4 (C_a-Cl (ii))	Cl	-0.46459	0	0	0		1.05158	0.88983	-15.29034		66.98	113.02	29.87	2.05530	0.34801
$-H_2C_bC_a-Cl$ (C_a-Cl (iii))	C_a	-0.72457	-0.92918	0	0	-153.26945	0.91771	0.82562	-16.47951	-16.28864	63.18	116.82	27.48	2.06384	0.37248
$-H_2C_bC_a-Cl$ (C_a-Cl (iii))	Cl	-0.72457	0	0	0		1.05158	0.87495	-15.55033		69.62	110.38	30.90	1.99599	0.30463
$C-H\ (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\ (CH)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ ($C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ ($C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.36. The energy parameters (eV) of functional groups of branched-chain alkyl chlorides.

Parameters	$C-Cl$ (i) Group	$C-Cl$ (ii) Group	$C-Cl$ (iii) Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	0.81317	0.81317	0.81317	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1	1
c_2	1	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	1	1	1	0	1	1	0	0	0	1	1	0
c_4	2	2	2	1	1	1	2	2	2	2	2	2
c_5	0	0	0	3	2	1	0	0	0	0	0	0
C_{1o}	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	0.81317	0.81317	0.81317	1	1	1	1	1	1	1	1	1
V_e (eV)	-29.68411	-28.95265	-29.68411	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	8.04432	7.96922	8.04432	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	6.38036	6.10748	6.38036	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_m (eV)	-3.19018	-3.05374	-3.19018	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(_{AO/HO})$ (eV)	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(_{AO/HO})$ (eV)	-1.44915	-0.92918	-1.44915	0	0	0	0	0	0	0	0	0
$E_T(_{AO/HO})$ (eV)	-13.18574	-13.70571	-13.18574	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(_{H_2MO})$ (eV)	-31.63536	-31.63540	-31.63536	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T\left(atom-atom,msp^3.AO\right)$ (eV)	-1.44915	-0.92918	-1.44915	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(_{MO})$ (eV)	-33.08452	-32.56455	-33.08452	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω $\left(10^{15}\ rad/s\right)$	7.42995	7.22380	13.0612	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	4.89052	4.75483	8.59708	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D$ (eV)	-0.14475	-0.14048	-0.19191	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}$ (eV)	0.08059 [12]	0.08059 [12]	0.09113 [13]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}$ (eV)	-0.10445	-0.10019	-0.14635	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mag} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(_{Group})$ (eV)	-33.18897	-32.66473	-33.23086	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(_{c_4\ AO/HO})$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(_{c_5\ AO/HO})$ (eV)	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(_{Group})$ (eV)	3.77116	3.39496	3.96108	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.37. The total bond energies of branched-chain alkyl chlorides calculated using the functional group composition and the energies of Table 15.36 compared to the experimental values [2]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_{D(Group)}$ (eV) values based on composition is given by (15.58).

Formula	Name	$C-Cl$ (i)	$C-Cl$ (ii)	$C-Cl$ (iii)	CH_3	CH_2	CH (i)	CH (ii)	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CCl_4	Tetrachloromethane	0	0	4	0	0	0	0	0	0	0	0	0	0	-1	13.43181	13.448	0.00123
$CHCl_3$	Trichloromethane	3	0	0	0	0	1	0	0	0	0	0	0	0	-1	14.49146	14.523	0.00217
CH_2Cl_2	Dichloromethane	2	0	0	0	1	0	0	0	0	0	0	0	0	0	15.37248	15.450	0.00499
CH_3Cl	Chloromethane	1	0	0	1	0	0	0	0	0	0	0	0	0	0	16.26302	16.312	0.00299
C_2H_5Cl	Chloroethane	0	0	1	1	1	0	0	0	1	0	0	0	0	0	28.61064	28.571	-0.00138
C_3H_7Cl	1-Chloropropane	0	0	1	1	2	0	0	2	0	0	0	0	0	0	40.76834	40.723	-0.00112
C_3H_7Cl	2-Chloropropane	0	0	1	2	0	1	0	0	2	0	0	0	0	0	40.86923	40.858	-0.00028
C_4H_9Cl	1-Chlorobutpane	0	0	1	1	3	0	0	3	0	0	0	0	0	0	52.92604	52.903	-0.00044
C_4H_9Cl	2-Chlorobutane	0	0	1	2	1	1	0	1	2	0	0	0	0	0	52.02693	52.972	-0.00104
C_4H_9Cl	1-Chloro-2-methylpropane	0	0	1	2	1	1	0	0	3	0	0	0	0	0	52.99860	52.953	-0.00085
C_4H_9Cl	2-Chloro-2-methylpropane	0	0	1	3	0	0	0	0	0	3	0	0	0	-1	53.21057	53.191	-0.00037
$C_5H_{11}Cl$	1-Chloropentane	0	0	1	1	4	0	0	4	0	0	0	0	0	0	65.08379	65.061	0.00034
$C_5H_{11}Cl$	1-Chloro-3-methylbutane	0	0	1	2	2	1	0	1	3	0	0	0	0	0	65.15630	65.111	-0.00069
$C_5H_{11}Cl$	2-Chloro-2-methylbutane	0	0	1	3	1	0	0	1	0	3	0	0	0	-1	65.36827	65.344	-0.00037
$C_5H_{11}Cl$	2-Chloro-3-methylbutane	0	0	1	3	0	2	0	0	3	0	1	0	0	0	65.16582	65.167	0.00002
$C_6H_{13}Cl$	2-Chlorohexane	0	0	1	2	3	1	0	3	2	0	0	0	0	0	77.34233	77.313	-0.00038
$C_8H_{17}Cl$	1-Chlorooctane	0	0	1	1	7	0	0	7	0	0	0	0	0	0	101.55684	101.564	0.00007
$C_{12}H_{25}Cl$	1-Chlorododecane	0	0	1	1	11	0	0	11	0	0	0	0	0	0	150.87640	150.202	0.00009
$C_{18}H_{37}Cl$	1-Chlorooctadecane	0	0	1	1	7	0	0	7	0	0	0	0	0	0	223.13384	223.175	0.00018

Table 15.38. The bond angle parameters of branched-chain alkyl chlorides and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle ClC_aCl$ $(C_a-Cl$ (i))	3.38271	3.38271	5.5889	-14.82575 Cl	1	-14.82575 Cl	1	0.91771	0.91771	1	0.81317 (Eq. (15.111))	1	0.91771	-0.92918				111.40	112.0 (dichloromethane) 111.3 (chloroform)
$\angle HC_aCl$ $(C_a-Cl$ (iii))	2.11106	3.38271	4.5961	-16.27490 C_a	15	-12.96764 Cl	Cl	0.83600	0.91771	0.75	0.95310 (Eq. (15.65))	0.75	1.09775	0				111.46	
$\angle HC_aH$ $\angle HC_bH$ $(C_a-Cl$ (iii))	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	109.2 ($\angle HC_aH$ ethyl chloride) 109.8 ($\angle HC_bH$ ethyl chloride)
$\angle C_aC_bH_b$ $(C_a-Cl$ (iii))															70.56			109.44	
$\angle C_bC_aCl$ $(C_a-Cl$ (iii))	2.91547	3.38271	5.1539	-15.75493 C_b	7	-12.96764 Cl	Cl	0.86359	0.86359	1	0.81317 (Eq. (15.111))	1	0.86359	-0.92918				109.61	110.7 (ethyl chloride) 111.0 (1,1-dichloroethane) 109.0 (1,2-dichloroethane) 109.6 (1,1,1-trichloroethane) 110.0 (hexachloroethane)
$\angle C_bC_aH_a$ $(C_a-Cl$ (iii))	2.91547	2.11106	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.83	110.6 (ethyl chloride)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

ALKYL BROMIDES ($C_nH_{2n+2-m}Br_m$, $n=1,2,3,4,5...\infty$ $m=1,2,3...\infty$)

The branched-chain alkyl bromides, $C_nH_{2n+2-m}Br_m$, may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds wherein at least one H is replaced by a bromine. The $C-Br$ bond comprises a functional group for each case of Br replacing a H of methane for the series $H_{4-m}C-Br_m$, $m=1,2,3$, with the $C-Br$ bond of CBr_4 comprising another functional group due to the limitation of the minimum energy of Br matched to that of the $C2sp^3$ HO. In addition, the $C-Br$ bond due to Br replacing a H of an alkane is a function group. The methyl, methylene, methylyne functional groups are equivalent to those of branched-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the $C-Br$ functional groups comprises the hybridization of the $2s$ and $2p$ shells of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ hybridized orbital (HO) and the Br AO to form a molecular orbital (MO) permits each participating orbital to decrease in radius and energy. In alkyl bromides, the energy of bromine is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_2 in Eq. (15.52) is one, and the energy matching condition is determined by the C_2 parameter. Then, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3)=-14.63489\ eV$ (Eq. (15.25)), and the Br AO has an energy of $E(Br)=-11.81381\ eV$. To meet the equipotential condition of the union of the $C-Br$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor C_2 of Eq. (15.52) for the $C-Br$-bond MO given by Eqs. (15.68) and (15.70) is

$$C_2(C2sp^3HO\ to\ Br)=\frac{E(Br)}{E(C,2sp^3)}c_2(C2sp^3HO)=\frac{-11.81381\ eV}{-14.63489\ eV}(0.91771)=0.74081 \quad (15.112)$$

The valence energy of the carbon $2p$ is $-11.2603\ eV$ and that of the Br AO is $-11.81381\ eV$. The energy difference is less than that of $E_T\left(C-C,2sp^3\right)$ given by Eq. (14.151) for a single bond. Thus, $E_T\left(atom-atom,msp^3.AO\right)$ of the alkyl $C-Br$-bond MO in Eq. (15.52) due to the charge donation from the C and Br atoms to the MO is $-0.92918\ eV$ (Eq. (14.513) based on the maximum single-bond-energy contribution of the $C2sp^3$ HO. $E_T\left(atom-atom,msp^3.AO\right)$ of the series CBr_mH_{4-m} $m=1,2,3$ is equivalent to those of methyl groups, $-0.72457\ eV$ (Eq. (14.151)). For CBr_4, $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-Br$-bond MO in Eq. (15.52) due to the charge donation from the C and Br atoms to the MO is $-0.36229\ eV$ (Eqs. (15.18-15.20 and Eq, (15.29) with a linear combination of $s=1$, $E_T\left(atom-atom,msp^3.AO\right)=-0.72457\ eV$ and $E_T\left(atom-atom,msp^3.AO\right)=0$) based on the maximum charge density on the $C2sp^3$ HO.

The symbols of the functional groups of branched-chain alkyl bromides are given in Table 15.39. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkyl bromides are given in Tables 15.40, 15.41, and 15.42, respectively. The total energy of each branched-chain alkyl bromide given in Table 15.43 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.42 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that was subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The $C-C$ bonds to the $CHBr$ group (one H bond to C) were each treated as an iso $C-C$ bond. The $C-C$ bonds to the CBr group (no H bonds to C) were each treated as a tert-butyl $C-C$. E_{mag} is subtracted for each t-butyl group. In the case of 2,3-dibromo-2-methylbutane, E_{mag} is positive since the terms due to the two bromine atoms cancel that of the t-butyl and CH groups. The bond angle parameters of branched-chain alkyl bromides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.112) are given in Table 15.44.

Table 15.39. The symbols of functional groups of branched-chain alkyl bromides.

Functional Group	Group Symbol
CBr of CBr_mH_{4-m}	$C-Br$ (i)
CBr of CBr_4	$C-Br$ (ii)
CBr of $C_nH_{2n+2-m}Br_m$	$C-Br$ (iii)
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.40. The geometrical bond parameters of branched-chain alkyl bromides and experimental values [1].

Parameter	$C-Br$ (i) Group	$C-Br$ (ii) Group	$C-Br$ (iii) Group	$C-H$ (CH_3) Group	$C-H$ (CH_2) Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
a (a_0)	2.49163	2.52509	2.47329	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
c' (a_0)	1.83395	1.84622	1.82719	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ $(Å)$	1.94097	1.95396	1.93381	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(Å)$	1.933 (methyl bromide)	1.935 (carbon tetrabromide)	1.93 (1,1,1-tribromoethane) 1.950 (1,2-dibromoethane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
b,c (a_0)	1.68667	1.72265	1.66689	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.73604	0.73115	0.73877	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.41. The MO to HO intercept geometrical bond parameters of branched-chain alkyl bromides. R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' $(°)$	θ_1 $(°)$	θ_2 $(°)$	d_1 (a_0)	d_2 (a_0)
$H_{4-m}C_a-Br_m$, $m=1,2,3$, $(C_a-Br$ (i))	C_a	-0.36229	0	0	0	-151.97798	0.91771	0.89582	-15.18804	-14.99717	68.10	111.90	29.52	2.16808	0.33413
$H_{4-m}C_a-Br_m$, $m=1,2,3$, $(C_a-Br$ (i))	Br	-0.36229	0	0	0		1.15169	0.89582	-15.18804		68.10	111.90	29.52	2.16808	0.33413
C_aBr_4 $(C_a-Br$ (ii))	C_a	-0.18114	0	0	0	-151.79683	0.91771	0.90664	-15.00689	-14.81603	66.10	113.90	28.76	2.21357	0.36734
C_aBr_4 $(C_a-Br$ (ii))	Br	-0.18114	0	0	0		1.15169	0.90664	-15.00689		66.10	113.90	28.76	2.21357	0.36734
$-H_2C_bC_aBr$ $(C_a-Br$ (iii))	C_a	-0.46459	-0.92918	0	0	-153.00946	0.91771	0.83885	-16.21952	-16.02866	62.67	117.33	26.55	2.21237	0.38518
$-H_2C_bC_aBr$ $(C_a-Br$ (iii))	Br	-0.46459	0	0	0		1.15169	0.88983	-15.29034		69.19	110.81	29.93	2.14337	0.31618
$C-H$ (CH_3)	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H$ (CH_2)	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H$ (CH)	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.42. The energy parameters (eV) of functional groups of branched-chain alkyl bromides.

Parameters	$C-Br$ (i) Group	$C-Br$ (ii) Group	$C-Br$ (iii) Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	0.74081	0.74081	0.74081	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1	1
c_2	1	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	0	0	1	1	0	0	0	1	1	0
c_4	2	2	2	1	1	1	2	2	2	2	2	2
c_5	0	0	0	3	2	1	0	0	0	0	0	0
C_{1o}	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	0.74081	0.74081	0.74081	1	1	1	1	1	1	1	1	1
V_e (eV)	-27.94806	-27.44996	-28.22940	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	7.41885	7.36953	7.44631	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	5.60839	5.43544	5.70686	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_m (eV)	-2.80419	-2.71772	-2.85343	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(AO/HO)$ (eV)	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(AO/HO)$ (eV)	-0.72457	-0.36229	-0.92918	0	0	0	0	0	0	0	0	0
$E_T(AO/HO)$ (eV)	-13.91032	-14.27260	-13.70571	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(H_2MO)$ (eV)	-31.63533	-31.63531	-31.63537	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom,msp^3.AO)$ (eV)	-0.72457	-0.36229	-0.92918	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(MO)$ (eV)	-32.35994	-31.99766	-32.56455	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω $(10^{15}\ rad/s)$	6.39733	6.27059	6.46864	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	4.21083	4.12741	4.25777	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D$ (eV)	-0.13137	-0.12861	-0.13293	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}$ (eV)	0.07575 [14]	0.08332 [15]	0.07575 [14]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}$ (eV)	-0.09349	-0.08695	-0.09506	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mag} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(Group)$ (eV)	-32.45343	-32.08460	-32.65961	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(c_4\ AO/HO)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(c_5\ AO/HO)$ (eV)	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(Group)$ (eV)	3.18365	2.81482	3.38983	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.43. The total bond energies of branched-chain alkyl bromides calculated using the functional group composition and the energies of Table 15.42 compared to the experimental values [2]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_{D(Group)}$ (eV) values based on composition is given by (15.58).

Formula	Name	$C-Br$ (i)	$C-Br$ (ii)	$C-Br$ (iii)	CH_3	CH_2	CH (i)	CH (ii)	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CBr_4	Tetrabromomethane	0	4	0	0	0	0	0	0	0	0	0	0	0	-1	11.25929	11.196	-0.00566
$CHBr_3$	Tribromomethane	3	0	0	0	0	1	0	0	0	0	0	0	0	0	12.87698	12.919	0.00323
CH_3Br	Bromomethane	1	0	0	1	0	0	0	0	0	0	0	0	0	0	15.67551	15.732	0.00360
C_2H_5Br	Bromoethane	0	0	1	1	1	0	0	1	0	0	0	0	0	0	28.03939	27.953	-0.00308
C_3H_7Br	1-Bromopropane	0	0	1	1	2	0	0	2	0	0	0	0	0	0	40.19709	40.160	-0.00093
C_3H_7Br	2-Bromopropane	0	0	1	2	0	1	0	0	2	0	0	0	0	0	40.29798	40.288	-0.00024
$C_5H_{10}Br_2$	2,3-Dibromo-2-methylbutane	1	0	0	3	0	1	0	0	1	2	0	0	2	0	68.48143	68.477	-0.00007
$C_6H_{13}Br$	1-Bromohexane	0	0	1	1	5	0	0	5	0	0	0	0	0	0	76.67019	76.634	-0.00047
$C_7H_{15}Br$	1-Bromoheptane	0	0	1	1	6	0	0	6	0	0	0	0	0	0	88.82789	88.783	0.00051
$C_8H_{17}Br$	1-Bromooctane	0	0	1	1	7	0	0	7	0	0	0	0	0	0	100.98559	100.952	-0.00033
$C_{12}H_{25}Br$	1-Bromododecane	0	0	1	1	11	0	0	11	0	0	0	0	0	0	149.61639	149.573	-0.00029
$C_{16}H_{33}Br$	1-Bromohexadecane	0	0	1	1	15	0	0	15	0	0	0	0	0	0	198.24719	198.192	-0.00028

Table 15.44. The bond angle parameters of branched-chain alkyl bromides and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle BrC_aBr$ (C_a-Br (i))	3.66790	3.66790	6.0816	-15.18804 Br	2	-15.18804 Br	2	0.89582	0.89582	1	0.74081 (Eq. (15.112))	1	0.89582	-0.92918				112.00	111.2 (methyl bromide) 113.2 (dibromomethane) 111.7 (bromoform)
$\angle HC_aBr$ (C_a-Br (iii))	2.11106	3.66790	4.8312	-15.55033 C_a	5	-11.81381 Br	Br	0.87495	0.91771	0.75	0.86829 (Eq. (15.65))	0.75	1.04887	0				110.53	109 (dibromomethane)
$\angle HC_aH$ $\angle HC_aH$ (C_a-Br (iii))	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bH_b$ (C_a-Br (iii))															70.56			109.44	110 (1,2-dibromoethane) 109.0 (1,1,1-tribromoethane)
$\angle C_bC_aBr$ (C_a-Br (iii))	2.91547	3.65437	5.4247	-15.75493 C_b	7	-11.81381 Br	Br	0.86359	0.86359	1	0.74081 (Eq. (15.112))	1	0.86359	-0.72457				110.82	109.5 (1,1-dibromoethane)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_bC_aC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

ALKYL IODIDES ($C_nH_{2n+2-m}I_m$, $n = 1,2,3,4,5...\infty$ $m = 1,2,3...\infty$)

The branched-chain alkyl iodides, $C_nH_{2n+2-m}I_m$, may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds wherein at least one H is replaced by an iodine atom. The $C-I$ bond comprises a functional group for I replacing a H of methane (CH_3I) or for I replacing a H of an alkane corresponding to the series $C_nH_{2n+2-m}I_m$. The $C-I$ bond of each of CH_2I_2 and CHI_3 comprise separate functional groups due to the limitation of the minimum energy of I matched to that of the $C2sp^3$ HO. The methyl, methylene, methylyne functional groups are equivalent to those of branched-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the $C-I$ functional groups comprises the hybridization of the $2s$ and $2p$ AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the I AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl iodides, the energy of iodine is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_2 in Eq. (15.52) is one, and the energy matching condition is determined by the C_2 parameter. Then, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3) = -14.63489\ eV$ (Eq. (15.25)). The I AO has an energy of $E(I) = -10.45126\ eV$. To meet the equipotential condition of the union of the $C-I$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor C_2 of Eq. (15.51) for the $C-I$-bond MO given by Eqs. (15.68) and (15.70) is

$$C_2(C2sp^3HO\ to\ I) = \frac{E(I)}{E(C,2sp^3)} c_2(C2sp^3HO) = \frac{-10.45126\ eV}{-14.63489\ eV}(0.91771) = 0.65537 \qquad (15.113)$$

The valence energy of the carbon $2p$ is $-11.2603\ eV$ and that of the I AO is $-10.45126\ eV$. The energy difference is positive. Thus, based on the maximum charge density on the $C2sp^3$

HO $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-I$-bond MO in Eq. (15.52) due to the charge donation from the C and I atoms to the MO is $-0.36229\ eV$ (Eqs. (15.18-15.20 and Eq. (15.29) with a linear combination of $s=1$, $E_T\left(atom-atom,msp^3.AO\right)=-0.72457\ eV$ and $E_T\left(atom-atom,msp^3.AO\right)=0$) for methyl and alkyl iodides, $-0.18114\ eV$ for diiodomethane, and 0 for CHI_3.

The symbols of the functional groups of branched-chain alkyl iodides are given in Table 15.45. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkyl iodides are given in Tables 15.46, 15.47, and 15.48, respectively. The total energy of each branched-chain alkyl iodide given in Table 15.49 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.48 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that was subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The $C-C$ bonds to the CHI group (one H bond to C) were each treated as an iso $C-C$ bond. The $C-C$ bonds to the CI group (no H bonds to C) were each treated as a tert-butyl $C-C$. E_{mag} is subtracted for each t-butyl group. The bond angle parameters of branched-chain alkyl iodides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.113) are given in Table 15.50.

Table 15.45. The symbols of functional groups of branched-chain alkyl iodides.

Functional Group	Group Symbol
CI of CH_3I and $C_nH_{2n+2-m}I_m$	$C-I$ (i)
CI of CH_2I_2	$C-I$ (ii)
CI of CHI_3	$C-I$ (iii)
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.46. The geometrical bond parameters of branched-chain alkyl iodides and experimental values [1].

Parameter	$C-I$ (i) Group	$C-I$ (ii) Group	$C-I$ (iii) Group	$C-H$ (CH_3) Group	$C-H$ (CH_2) Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
a (a_0)	2.67103	2.68865	2.70662	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
c' (a_0)	2.01881	2.02546	2.03222	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ $(\AA)$	2.13662	2.14365	2.15081	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(\AA)$	2.132 (methyl iodide)	2.132 (methyl iodide)	2.15 (carbon tetraiodide)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
b,c (a_0)	1.74894	1.76815	1.78770	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.75582	0.75334	0.75083	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.47. The MO to HO intercept geometrical bond parameters of branched-chain alkyl iodides. R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
CH_3I $(C_a-I$ (i))	C_a	-0.18114	0	0	0	-151.79683	0.91771	0.90664	-15.00689	-14.81603	69.63	110.37	29.08	2.33442	0.31560
CH_3I $(C_a-I$ (i))	I	-0.18114	0	0	0		1.30183	0.90664	-15.00689		69.63	110.37	29.08	2.33442	0.31560
$-H_2C_bC_aI$ $(C_a-I$ (i))	C_a	-0.18114	-0.92918	0	0	-152.72602	0.91771	0.85377	-15.93608	-15.74521	63.16	116.84	25.82	2.40436	0.38554
$-H_2C_bC_aI$ $(C_a-I$ (i))	I	-0.18114	0	0	0		1.30183	0.90664	-15.00689		69.63	110.37	29.08	2.33442	0.31560
$C_aH_2I_2$ $(C_a-I$ (ii))	C_a	-0.09057	0	0	0	-151.70626	0.91771	0.91214	-14.91632	-14.72546	68.61	111.39	28.71	2.35818	0.33272
$C_aH_2I_2$ $(C_a-I$ (ii))	I	-0.09057	0	0	0		1.30183	0.91214	-14.91632		68.61	111.39	28.71	2.35818	0.33272
C_aHI_3 $(C_a-I$ (iii))	C_a	0	0	0	0	-151.61569	0.91771	0.91771	-14.82575	-14.63489	67.56	112.44	28.32	2.38256	0.35035
C_aHI_3 $(C_a-I$ (iii))	I	0	0	0	0		1.30183	0.91771	-14.82575	-14.63489	67.56	112.44	28.32	2.38256	0.35035
$C-H$ (CH_3)	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H$ (CH_2)	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H$ (CH)	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.48. The energy parameters (eV) of functional groups of branched-chain alkyl iodides.

Parameters	$C-I$ (i) Group	$C-I$ (ii) Group	$C-I$ (iii) Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	0.65537	0.65537	0.65537	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1	1
c_2	1	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	1	0	1	0	1	1	0	0	0	1	1	0
c_4	2	2	2	1	1	1	2	2	2	2	2	2
c_5	0	0	0	3	2	1	0	0	0	0	0	0
C_{1o}	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	0.65537	0.65537	0.65537	1	1	1	1	1	1	1	1	1
$V_e\ (eV)$	-26.59109	-26.34902	-26.10696	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_p\ (eV)$	6.73951	6.71739	6.69505	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
$T\ (eV)$	4.97768	4.90005	4.82280	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$V_m\ (eV)$	-2.48884	-2.45002	-2.41140	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(_{AO/HO})\ (eV)$	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(_{AO/HO})\ (eV)$	-0.36229	-0.18114	0	0	0	0	0	0	0	0	0	0
$E_T(_{AO/HO})\ (eV)$	-14.29907	-14.45375	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(_{H_2MO})\ (eV)$	-31.63534	-31.63535	-31.63540	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom,msp^3.AO)\ (eV)$	-0.36229	-0.18114	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(_{MO})\ (eV)$	-31.99766	-31.81651	-31.63537	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\ (10^{15}\ rad/s)$	10.2318	5.36799	9.90080	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_K\ (eV)$	6.73472	3.53331	6.51688	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D\ (eV)$	-0.16428	-0.11832	-0.15977	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}\ (eV)$	0.06608 [16]	0.06608 [16]	0.06608 [16]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}\ (eV)$	-0.13124	-0.08527	-0.12673	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{mag}\ (eV)$	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(_{Group})\ (eV)$	-32.12889	-31.90179	-31.76210	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(_{c_4\ AO/HO})\ (eV)$	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(_{c_5\ AO/HO})\ (eV)$	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(_{Group})\ (eV)$	2.71108	2.63201	2.34429	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.49. The total bond energies of branched-chain alkyl iodides calculated using the functional group composition and the energies of Table 15.48 compared to the experimental values [2]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(_{Group})\ (eV)$ val based on composition is given by (15.58).

Formula	Name	$C-I$ (i)	$C-I$ (ii)	$C-I$ (iii)	CH_3	CH_2	CH (i)	CH (ii)	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CHI_3	Triiodomethane	0	0	3	0	0	1	0	0	0	0	0	0	0	0	10.35888	10.405	0.00444
CH_2I_2	Diiodomethane	0	2	0	0	1	0	0	0	0	0	0	0	0	-1	12.94614	12.921	-0.00195
CH_3I	Iodomethane	1	0	0	1	0	0	0	0	0	0	0	0	0	0	15.20294	15.163	-0.00263
C_2H_5I	Iodoethane	1	0	0	1	1	0	0	1	0	0	0	0	0	0	27.36064	27.343	-0.00066
C_3H_7I	1-Iodopropane	1	0	0	1	2	0	0	2	0	0	0	0	0	0	39.51834	39.516	-0.00006
C_3H_7I	2-Iodopropane	1	0	0	2	0	1	0	0	2	0	0	0	0	0	39.61923	39.623	0.00009
C_4H_9I	2-Iodo-2-methylpropane	1	0	0	3	0	0	0	0	0	3	0	0	0	-1	51.96057	51.899	-0.00119

Table 15.50. The bond angle parameters of branched-chain alkyl iodides and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle IC_aI$ $(C_a-I\ (ii))$	4.05092	4.05092	6.7205	-10.45126 I	1	-10.45126 I	1	1	1	1	0.65537 (Eq. (15.113))	1	1	-0.36228				112.10	
$\angle HC_aI$ $(C_a-I\ (i))$	2.11106	4.03763	5.2203	-14.82575 C_a	1	-10.45126 I	1	0.91771	0.91771	0.75	0.76815 (Eq. (15.65))	0.75	1.00000	0				112.39	
$\angle HC_aH$ $\angle HC_bH$ $(C_a-I\ (i))$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	111.2 (methyl iodide)
$\angle C_aC_bH_b$ $(C_a-I\ (i))$															70.56			109.44	
$\angle C_bC_aI$ $(C_a-I\ (i))$	2.91547	4.03763	5.7939	-15.55033 C_b	5	-10.45126 I	1	0.87495	0.87495	1	0.65537 (Eq. (15.113))	1	0.87495	-0.36228				111.86	
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

ALKENYL HALIDES ($C_nH_{2n-m}X_m$, $n = 3,4,5...\infty$ $m = 1,2,3...\infty$)

The branched-chain alkenyl halides, $C_nH_{2n+2-m}X_m$ with $X = F,Cl,Br,I$, may comprise alkyl and alkenyl functional groups wherein at least one H is replaced by a halogen atom. In the case that a halogen atom replaces an alkyl H, the $C-X$ bond comprises the alkyl-halogen functional groups given in their respective sections. The alkenyl halogen $C-X$ bond comprises a separate functional group for each case of X bonding to the $C=C$-bond functional group given in the Alkenes section. In addition the CH group of the moiety $XCH=C$ comprises a functional group unique to alkenyl halides. The straight and branched-chain alkenes, C_nH_{2n}, comprise at least one carbon-carbon double bond comprising a functional group that is solved equivalently to the double bond of ethylene. The double bond may be bound to one, two, three, or four carbon single bonds that substitute for the hydrogen atoms of ethylene. The three distinct functional groups given in the Alkenes section are C vinyl single bond to $-C(C)=C$, C vinyl single bond to $-C(H)=C$, and C vinyl single bond to $-C(C)=CH_2$. In addition, CH_2 of the $-C=CH_2$ moiety is also an alkene functional group solved in the Alkenes section.

Consider the case where $X=Cl$ substitutes for a carbon single bond or a hydrogen atom. Based on the condition of energy matching of the orbital, any magnetic energy due to unpaired electrons in the constituent fragments, and differences in oscillation in the transition state, two distinct $C-Cl$ functional groups can be identified: Cl vinyl single bond to $-C(C)=C$ and Cl vinyl single bond to $-C(H)=C$. The alkenyl-halide CH group is equivalent to that solved in the Hydrogen Carbide (CH) section except that $\Delta E_{H_2MO}(AO/HO) = -1.13379\ eV$ in order to energy match to the $C-Cl$ and $C=C$ bonds.

The alkyl portion of the alkenyl halide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in alkene halides are equivalent to those in branched-chain alkanes.

$E_T\left(atom-atom,msp^3.AO\right)$ of the $C=C$-bond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is equivalent to that of ethylene, $-2.26759\ eV$, given by Eq. (14.247). $E_T\left(atom-atom,msp^3.AO\right)$ of each $C-C$-bond MO in Eq. (15.52) is $-1.85836\ eV$ or $-1.44915\ eV$ based on the energy match between the $C2sp^3$ HOs corresponding to the energy contributions equivalent to those of methylene, $-0.92918\ eV$ (Eq. (14.513), or methyl, $-0.72457\ eV$ (Eq. (14.151)), groups, respectively.

The solution of each $C-X$ functional group comprises the hybridization of the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the X AO to form a MO permits each participating orbital to decrease in radius and energy. The alkenyl $C-X$-bond functional groups comprise single bonds and are equivalent to those of the corresponding alkyl halides except that the halogen AO and the $C-X$-bond MO are each energy matched to the alkene $C2sp^3$ HO. In alkenyl halides with $X=Cl,Br,\ or\ I$, the energy of the halogen atom is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_2 in Eq. (15.52) is one, and the energy matching condition is determined by the C_2 parameter. For example, the hybridization factor C_2 of Eq. (15.52) for the alkenyl $C-Cl$-bond MO given by Eq. (15.111) is $C_2\left(C2sp^3HO\ to\ \mathrm{Cl}\right)=0.81317$.

$E_T\left(atom-atom,msp^3.AO\right)$ of the alkenyl $C-Cl$-bond MO in Eq. (15.52) due to the charge donation from the C and Cl atoms to the MO is $-0.72457\ eV$ for the Cl vinyl single bond to $-C(H)=C\quad C-Cl$ group and $-0.92918\ eV$ for the Cl vinyl single bond to $-C(C)=C\quad C-Cl$ group. It is based on the energy match between the Cl atom and the $C2sp^3$ HO of an unsubstituted vinyl group and a substituted vinyl group given by Eqs. (14.151) and (14.513), respectively.

The symbols of the functional groups of branched-chain alkenyl chlorides are given in Table 15.51. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkenyl chlorides are given in Tables 15.52, 15.53, and 15.54, respectively. The total energy of each branched-chain alkenyl chloride given in Table 15.55 was calculated as the sum over the integer multiple of each $E_D(_{Group})$ of Table 15.54 corresponding to functional-group composition of the molecule.

The bond angle parameters of branched-chain alkenyl chlorides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.111) are given in Table 15.56.

Table 15.51. The symbols of functional groups of branched-chain alkenyl chlorides.

Functional Group	Group Symbol
Cl vinyl single bond to -C(H)=C	$C-Cl$ (i)
Cl vinyl single bond to -C(C)=C	$C-Cl$ (ii)
CC double bond	$C=C$
C vinyl single bond to -C(C)=C	$C-C$ (i)
C vinyl single bond to -C(H)=C	$C-C$ (ii)
C vinyl single bond to -C(C))=CH_2	$C-C$ (iii)
CH (alkenyl halide)	$C-H$ (i)
CH_2 alkenyl group	$C-H\ (CH_2)$ (i)
CH_3 group	$C-H\ (CH_3)$
CH_2 alkyl group	$C-H\ (CH_2)$ (ii)
CH (alkyl)	$C-H$ (ii)
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.52. The geometrical bond parameters of branched-chain alkenyl chlorides and experimental values [1].

Parameter	$C-Cl$ (i) Group	$C-Cl$ (ii) Group	$C=C$ Group	$C-C$ (i) Group	$C-C$ (ii) Group	$C-C$ (iii) Group	$C-H\ (CH_2)$ (i) Group	$C-H$ (i) Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ (ii) Group	$C-H$ (ii) Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	2.15818	2.19358	1.47228	2.04740	2.04740	2.04740	1.64010	1.60061	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.62912	1.64243	1.26661	1.43087	1.43087	1.43087	1.04566	1.03299	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ (Å)	1.72419	1.73827	1.34052	1.51437	1.51437	1.51437	1.10668	1.09327	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.730 (vinyl chloride) 1.73 (1,1-dichloroethylene)	1.730 (vinyl chloride) 1.73 (1,1-dichloroethylene)	1.342 (2-methylpropene) 1.346 (2-butene) 1.349 (1,3-butadiene)		1.508 (2-butene)	1.508 (2-methylpropene)	1.10 (2-methylpropene) 1.108 (avg.) (1,3-butadiene)	1.09 (vinyl chloride)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	1.41552	1.45403	0.75055	1.46439	1.46439	1.46439	1.26354	1.22265	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.75486	0.74874	0.86030	0.69887	0.69887	0.69887	0.63756	0.64537	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.53. The MO to HO intercept geometrical bond parameters of branched-chain alkenyl chlorides. R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C'_b=C'_a(Cl)-H$ (CH) (i)	C'_a	-1.34946	-0.72457	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	76.99	103.01	40.53	1.21653	0.18354
$-C'_b=C'_a(H)Cl$ $(C'_a-Cl$ (i))	C'_a	-1.13379	-0.72457	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	79.43	100.57	34.49	1.77872	0.14960
$-C'_b=C'_a(H)Cl$ $(C'_a-Cl$ (i))	Cl	-0.72457	0	0	0		1.05158	0.87495	-15.55033		85.36	94.64	38.03	1.69995	0.07083
$-C'_b=C'_a(C')Cl$ $(C'_a-Cl$ (ii))	C'_a	1.13379	-0.46459	-0.92918	0	-154.14326	0.91771	0.78405	-17.35332	-17.16245	72.17	107.83	30.88	1.88253	0.24010
$-C'_b=C'_a(C)Cl$ $(C'_a-Cl$ (ii))	Cl	-0.46459	0	0	0		1.05158	0.88983	-15.29034		83.62	96.38	37.46	1.74125	0.09882
$C'_c(H)C'_a=C'_aH,C'_d$	C'_a	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	127.61	52.39	58.24	0.77492	0.49168
$C'_c(H)C'_a=C'_bH_2$	C'_b	-1.13380	0	0	0	-152.74949	0.91771	0.85252	-15.95955	-15.76868	129.84	50.16	60.70	0.72040	0.54620
$C'_c(C'_d)C'_a=C'_bH,C'_e$	C'_a	-1.13380	-0.72457	-0.72457	0	-154.19863	0.91771	0.78155	-17.40869	-17.21783	126.39	53.61	56.95	0.80289	0.46371
$R_1C'_bH_2-C'_a(C')=C'$ $(C'-C'$ (i))	C'_a	-1.13380	-0.72457	-0.72457	0	-154.19863	0.91771	0.78155	-17.40869	-17.21783	60.88	119.12	27.79	1.81127	0.38039
$R_1C'_bH_2-C'_a(C')=C'$ $(C'-C'$ (i)) $R_1C'_bH_2-C'_a(C')=CH_2$ $(C-C$ (iii))	C'_b	-0.72457	-0.92918	0	0	-153.26945	0.91771	0.82562	-16.47951	-16.28864	67.40	112.60	31.36	1.74821	0.31734
$R_1C'_bH_2-C'_a(H)=C'$ $(C'-C'$ (ii))	C'_a	-1.13380	-0.92918	0	0	-153.67866	0.91771	0.80561	-16.88873	-16.69786	64.57	115.43	29.79	1.77684	0.34596
$R_1C'_bH_2-C'_a(H)=C'$ $(C'-C'$ (i))	C'_b	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	65.99	114.01	30.58	1.76270	0.33183
$C'-H$ (CH_2) (i)	C'	-1.13380	0	0	0	-152.74949	0.91771	0.85252	-15.95955	-15.76868	77.15	102.85	41.13	1.23531	0.18965
$C'-H$ (CH_3)	C'	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C'-H$ (CH_2) (ii)	C'	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C'-H$ (CH) (ii)	C'	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C'_aC'_bH_2CH_2-$ $(C'-C'$ (a))	C'_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C'_aC'_bH_2CH_2-$ $(C'-C'$ (a))	C'_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C'_aC'_b(H_2C'_c-R')HCH_2-$ $(C'-C'$ (b))	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C'_a(R'-H_2C'_d)C'_b(R''-H_2C'_c)CH_2-$ $(C'-C'$ (c))	C'_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC'_aC'_b(H_2C'_c-R')HCH_2-$ $(C'-C'$ (d))	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC'_a(R'-H_2C'_d)C'_b(R''-H_2C'_c)CH_2-$ $(C'-C'$ (e))	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC'_aC'_b(H_2C'_c-R')HCH_2-$ $(C'-C'$ (f))	C'_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC'_a(R'-H_2C'_d)C'_b(R''-H_2C'_c)CH_2-$ $(C'-C'$ (f))	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.54. The energy parameters (eV) of functional groups of branched-chain alkenyl chlorides.

Parameters	$C-Cl$ (i) Group	$C-Cl$ (ii) Group	$C=C$ Group	$C-C$ (i) Group	$C-C$ (ii) Group	$C-C$ (iii) Group	CH_2 (i) Group	$C-H$ (i) Group	CH_3 Group	CH_2 (ii) Group	$C-H$ (ii) Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	1	2	1	1	1	2	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	0	0	0	1	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	0.81317	0.81317	0.91771	1	1	1	1	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
c_2	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	1	0	0	1	0	1	1	1	0	1	1	0	0	0	1	1	0
c_4	2	2	4	2	2	2	1	1	1	1	1	2	2	2	2	2	2
c_5	0	0	0	0	0	0	2	1	3	2	1	0	0	0	0	0	0
C_{1o}	0.5	0.5	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	0.81317	0.81317	0.91771	1	1	1	1	1	1	1	1	1	1	1	1	1	1
V_e (eV)	-32.87721	-32.14474	-102.08992	-30.19634	-30.19634	-30.19634	-72.03287	-37.10024	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	8.35160	8.28394	21.48386	9.50874	9.50874	9.50874	26.02344	13.17125	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	7.61688	7.32700	34.67062	7.37432	7.37432	7.37432	21.95990	11.58941	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_m (eV)	-3.80844	-3.66350	-17.33531	-3.68716	-3.68716	-3.68716	-10.97995	-5.79470	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(_{AO/HO})$ (eV)	-14.63489	-14.63489	0	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(_{AO/HO})$ (eV)	-3.71674	-3.19677	0	0	0	0	0	-1.13379	0	0	0	0	0	0	0	0	0
$E_T(_{AO/HO})$ (eV)	-10.91815	-10.97139	0	-14.63489	-14.63489	-14.63489	-14.63489	-13.50110	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(_{H_2MO})$ (eV)	-31.63531	-31.63541	-63.27075	-31.63534	-31.63534	-31.63534	-49.66437	-31.63539	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom, msp^3.AO)$ (eV)	-1.44915	-0.92918	-2.26759	-1.44915	-1.85836	-1.44915	0	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(_{MO})$ (eV)	-33.08452	-32.56455	-65.53833	-33.08452	-33.49373	-33.08452	-49.66493	-31.63537	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω $(10^{15}\ rad/s)$	8.31434	8.11389	43.0680	9.97851	16.4962	9.97851	25.2077	26.4826	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	5.47264	5.34070	28.34813	6.56803	10.85807	6.56803	16.59214	17.43132	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D$ (eV)	-0.15312	-0.14888	-0.34517	-0.16774	-0.21834	-0.16774	-0.25493	-0.26130	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}$ (eV)	0.08059 [12]	0.08059 [12]	0.17897 [6]	0.15895 [7]	0.09931 [8]	0.09931 [8]	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}$ (eV)	-0.11282	-0.10859	-0.25568	-0.08827	-0.16869	-0.11809	-0.07727	-0.08364	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mag} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(_{Group})$ (eV)	-33.19734	-32.67314	-66.04969	-33.17279	-33.66242	-33.20260	-49.81948	-31.71901	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(_{c_4\ AO/HO})$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(_{c_5\ AO/HO})$ (eV)	0	0	0	0	0	0	-13.59844	-13.59844	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(_{Group})$ (eV)	3.77953	3.40336	7.51014	3.75498	4.39264	3.78480	7.83968	3.33765	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.55. The total bond energies of branched-chain alkenyl chlorides calculated using the functional group composition and the energies of Table 15.54 compared to the experimental values [2].

Formula	Name	$C-Cl$ (i)	$C-Cl$ (ii)	$C=C$	$C-C$ (i)	$C-C$ (ii)	$C-C$ (iii)	CH_2 (i)	CH (i)	CH_3	CH_2 (ii)	CH (ii)	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_3Cl	Chloroethene	1	0	1	0	0	0	1	1	0	0	0	0	0	0	0	0	0	22.46700	22.505	0.00170
C_3H_5Cl	2-Chloropropene	0	1	1	0	0	1	1	0	1	0	0	0	0	0	0	0	0	35.02984	35.05482	0.00071

Table 15.56. The bond angle parameters of branched-chain alkenyl chlorides and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom, msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_o)	$2c'$ Bond 2 (a_o)	$2c'$ Terminal Atoms (a_o)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HC_aCl$ $(C_a-Cl\ (i))$	2.06598	3.25825	4.5809	-16.27490 C_a	15	-12.96764 Cl	Cl	0.83600	0.91771	0.75	0.95310 (Eq. (15.65))	0.75	1.09775	0				116.94	
$\angle C_b=C_aH$ $(C_a-Cl\ (i))$																116.94		121.53	124 (vinyl chloride)
$\angle C_b=C_aCl$ $(C_a-Cl\ (i))$																116.94		121.53	122.5 (vinyl chloride) 123.8 (1,1-dichloroethylene)
$\angle C_b=C_aCl$ $(C_a-Cl\ (i))$	2.53321	3.25825	5.1060	-15.75493 C_b	7	-12.96764 Cl	Cl	0.86359	0.86359	1	0.81317 (Eq. (15.111))	1	0.86359	-0.92918				123.19	123.8 (1,1-dichloroethylene) 122.5 (vinyl chloride)
$\angle HC_aC_c$ $(C_c(H)C_a=C_b)$	2.11323	2.86175	4.2895	-15.95954 C_a	9	-14.82575 C_c	1	0.85252	0.91771	0.75	1	0.75	1.07647	0				118.36	
$\angle C_cC_aC_c$ $(C_c(C_c)C_a=C_b)$	2.86175	2.86175	4.7958	-16.68411 C_c	24	-16.68411 C_c	24	0.81549	0.81549	1	1	1	0.81549	-1.85836				113.84	
$\angle C_bC_aC_c$ $(C_b=C_aC_c)$	2.53321	2.86175	4.7539	-16.88873 C_b		-16.68411 C_c	24	0.80561	0.81549	1	1	1	0.81055	-1.85836				123.46	124.4 (1,3,5-hexatriene CbCcCc) 121.7 (1,3,5-hexatriene CaCbCc) 124.4 (1,3-butadiene CCC) 125.3 (2-butene CbCaCc)
$\angle HC_aC_b$																118.36	123.46	118.19	
$\angle HC_aH$ $(H_2C_a=C_bC_c)$	2.04578	2.04578	3.4756	-15.95955	9	H	H	0.85252	1	1	1	0.75	1.17300	0				116.31	118.5 (2-methylpropene)
$\angle C_bC_aH$ $(H_2C_a=C_bC_c)$																116.31		121.85	121 (2-methylpropene)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

ALCOHOLS ($C_nH_{2n+2}O_m$, $n = 1,2,3,4,5...\infty$)

The alkyl alcohols, $C_nH_{2n+2}O_m$, comprise an OH functional group and two types of $C-O$ functional groups, one for methyl alcohol and the other for general alkyl alcohols. The alkyl portion of the alkyl alcohol may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2 CH$) and t-butyl ($(CH_3)_3 C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in alcohols are equivalent to those in branched-chain alkanes.

The OH functional group was solved in the Hydroxyl Radical (OH) section. Each $C-O$ group is solved by hybridizing the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the O AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl alcohols, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3) = -14.63489\ eV$ (Eq. (15.25)) and the O AO has an energy of $E(O) = -13.61806\ eV$. To meet the equipotential condition of the union of the $C-O$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the $C-O$-bond MO given by Eqs. (15.68) and (15.70) is

$$c_2\left(C2sp^3HO \ to \ O\right) = \frac{E(O)}{E\left(C,2sp^3\right)} c_2\left(C2sp^3HO\right) = \frac{-13.61806\ eV}{-14.63489\ eV}(0.91771) = 0.85395 \quad (15.114)$$

$E_T\left(atom-atom,msp^3.AO\right)$ of the $C-O$-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is $-1.65376\ eV$ for the CH_3-OH $C-O$ group. It is based on the energy match between the OH group and the $C2sp^3$ HO of a methyl group and is given by the linear combination of $-0.92918\ eV$ (Eq. (14.513)) and $-0.72457\ eV$ (Eq. (14.151)), respectively. For the alkyl $C-O$ group, $E_T\left(atom-atom,msp^3.AO\right)$ is $-1.85836\ eV$. It is based on the energy match between the O AO and the $C2sp^3$ HO of a methylene group where both energy contributions are given by Eq. (14.513).

The symbols of the functional groups of branched-chain alkyl alcohols are given in Table 15.57. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl alcohols are given in Tables 15.58, 15.59, and 15.60, respectively. The total energy of each alkyl alcohol given in Table 15.61 was calculated as the sum over the integer multiple of each $E_D(_{Group})$ of Table 15.60 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl alcohols determined using Eqs. (15.79-15.108) are given in Table 15.62.

Table 15.57. The symbols of functional groups of alkyl alcohols.

Functional Group	Group Symbol
OH group	OH
CH_3OH C-O	$C-O$ (i)
Alkyl C-O	$C-O$ (ii)
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.58. The geometrical bond parameters of alkyl alcohols and experimental values [1].

Parameter	OH Group	$C-O$ (i) Group	$C-O$ (ii) Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.26430	1.79473	1.78255	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	0.91808	1.33968	1.33512	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ (Å)	0.971651	1.41785	1.41303	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	0.971 (ethanol) 0.9451 (methanol)	1.4246 (methanol)	1.431 (ethanol)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	0.86925	1.19429	1.18107	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.72615	0.74645	0.74900	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.59. The MO to HO intercept geometrical bond parameters of alkyl alcohols. R, R', R'' are H or alkyl groups. E_T is $E_T(atom-atom, msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
H_3CO-H	O	-0.82688	0	0	0		1.00000	0.86923	-15.65263		115.49	64.51	64.51	0.54405	0.37403
$-H_2C_aO-H$	O	-0.92918	0	0	0		1.00000	0.86359	-15.75493		115.09	64.91	64.12	0.55182	0.36625
H_3C-OH $(C-O$ (i))	C'	-0.82688	0	0	0	-152.44257	0.91771	0.86923	-15.65263	-15.46177	96.59	83.41	46.30	1.23986	0.09981
H_3C-OH $(C-O$ (i))	O	-0.82688	0	0	0		1.00000	0.86923	-15.65263		96.59	83.41	46.30	1.23986	0.09981
$-H_2C_a-OH$ $(C-O$ (ii))	C'_a	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	93.09	86.91	43.59	1.29114	0.04398
$-H_2C_a-OH$ $(C-O$ (ii))	O	-0.92918	0	0	0		1.00000	0.86359	-15.75493		97.20	82.80	46.50	1.22692	0.10820
$C'-H\ (CH_3)$	C'	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C'-H\ (CH_2)$	C'	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C'-H\ (CH)$	C'	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C'_aC'_bH_2CH_2-$ $(C'-C'$ (a))	C'_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C'_aC'_bH_2CH_2-$ $(C'-C'$ (a))	C'_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C'_aC'_b(H_2C'_c-R')HCH_2-$ $(C'-C'$ (b))	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C'_a(R'-H_2C'_d)C'_b(R''-H_2C'_c)CH_2-$ $(C'-C'$ (c))	C'_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC'_aC'_b(H_2C'_c-R')HCH_2-$ $(C'-C'$ (d))	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC'_a(R'-H_2C'_d)C'_b(R''-H_2C'_c)CH_2-$ $(C'-C'$ (e))	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC'_aC'_b(H_2C'_c-R')HCH_2-$ $(C'-C'$ (f))	C'_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC'_a(R'-H_2C'_d)C'_b(R''-H_2C'_c)CH_2-$ $(C'-C'$ (f))	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.60. The energy parameters (eV) of functional groups of alkyl alcohols.

Parameters	OH Group	$C-O$ (i) Group	$C-O$ (ii) Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.75	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1	1	1	1
c_1	0.75	1	1	1	1	1	1	1	1	1	1	1
c_2	1	0.85395	0.85395	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	1	0	0	0	1	1	0	0	0	1	1	0
c_4	1	2	2	1	1	1	2	2	2	2	2	2
c_5	1	0	0	3	2	1	0	0	0	0	0	0
C_{1o}	0.75	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	1	1	1	1	1	1	1	1	1	1	1	1
V_e (eV)	-40.92709	-33.47304	-33.78820	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	14.81988	10.15605	10.19068	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	16.18567	9.32537	9.47749	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_m (eV)	-8.09284	-4.66268	-4.73874	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(_{AO/HO})$ (eV)	-13.6181	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(_{AO/HO})$ (eV)	0	-1.65376	-1.85836	0	0	0	0	0	0	0	0	0
$E_T(_{AO/HO})$ (eV)	-13.6181	-12.98113	-12.77653	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(_{H_2MO})$ (eV)	-31.63247	-31.63544	-31.63529	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom, msp^3.AO)$ (eV)	0	-1.65376	-1.85836	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(_{MO})$ (eV)	-31.63537	-33.28912	-33.49373	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω $(10^{15}$ $rad/s)$	44.1776	22.3978	12.2831	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	29.07844	14.74264	8.08494	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D$ (eV)	-0.33749	-0.25287	-0.18841	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}$ (eV)	0.46311 [17-18]	0.12808 [19]	0.13328 [20]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}$ (eV)	-0.10594	-0.18883	-0.12177	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mag} (eV)	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(_{Group})$ (eV)	-31.74130	-33.47795	-33.61550	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(_{c_4}$ $_{AO/HO})$ (eV)	-13.6181	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(_{c_5}$ $_{AO/HO})$ (eV)	-13.59844	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(_{Group})$ (eV)	4.41035	4.20817	4.34572	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.61. The total bond energies of alkyl alcohols calculated using the functional group composition and the energies of Table 15.60 compared to the experimental values [3].

Formula	Name	OH Group	$C-O$ (i) Group	$C-O$ (ii) Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_4O	Methanol	1	0	1	1	0	0	0	0	0	0	0	0	21.11038	21.131	0.00097
C_2H_6O	Ethanol	1	0	1	1	1	0	1	0	0	0	0	0	33.40563	33.428	0.00066
C_3H_8O	1-Propanol	1	0	1	1	2	0	2	0	0	0	0	0	45.56333	45.584	0.00046
C_3H_8O	2-Propanol	1	0	1	2	0	1	2	0	0	0	0	0	45.72088	45.766	0.00098
$C_4H_{10}O$	1-Butanol	1	0	1	1	3	0	3	0	0	0	0	0	57.72103	57.736	0.00026
$C_4H_{10}O$	2-Butanol	1	0	1	2	1	1	3	0	0	0	0	0	57.87858	57.922	0.00074
$C_4H_{10}O$	2-Methyl-1-propananol	1	0	1	2	1	1	0	3	0	0	0	0	57.79359	57.828	0.00060
$C_4H_{10}O$	2-Methyl-2-propananol	1	0	1	3	0	0	0	0	3	0	0	0	58.15359	58.126	-0.00048
$C_5H_{12}O$	1-Pentanol	1	0	1	1	4	0	4	0	0	0	0	0	69.87873	69.887	0.00011
$C_5H_{12}O$	2-Pentanol	1	0	1	2	2	1	4	0	0	0	0	0	70.03628	70.057	0.00029
$C_5H_{12}O$	3-Pentanol	1	0	1	2	2	1	4	0	0	0	0	0	70.03628	70.097	0.00087
$C_5H_{12}O$	2-Methyl-1-butananol	1	0	1	2	2	1	2	3	0	0	0	0	69.95129	69.957	0.00008
$C_5H_{12}O$	3-Methyl-1-butananol	1	0	1	2	2	1	1	3	0	0	0	0	69.95129	69.950	-0.00002
$C_5H_{12}O$	2-Methyl-2-butananol	1	0	1	3	1	0	1	0	3	0	0	0	70.31129	70.246	-0.00092
$C_5H_{12}O$	3-Methyl-2-butananol	1	0	1	3	0	2	0	3	0	1	0	0	69.96081	70.083	0.00174
$C_6H_{14}O$	1-Hexanol	1	0	1	1	5	0	5	0	0	0	0	0	82.03643	82.054	0.00021
$C_6H_{14}O$	2-Hexanol	1	0	1	2	3	1	5	0	0	0	0	0	82.19398	82.236	0.00052
$C_7H_{16}O$	1-Heptanol	1	0	1	1	6	0	6	0	0	0	0	0	94.19413	94.214	0.00021
$C_8H_{18}O$	1-Octanol	1	0	1	1	7	0	7	0	0	0	0	0	106.35183	106.358	0.00006
$C_8H_{18}O$	2-Ethyl-1-hexananol	1	0	1	2	13	1	4	3	0	0	0	0	106.42439	106.459	0.00032
$C_9H_{20}O$	1-Nonanol	1	0	1	1	8	0	8	0	0	0	0	0	118.50953	118.521	0.00010
$C_{10}H_{22}O$	1-Decanol	1	0	1	1	9	0	9	0	0	0	0	0	130.66723	130.676	0.00007
$C_{12}H_{26}O$	1-Dodecanol	1	0	1	1	11	0	11	0	0	0	0	0	154.98263	154.984	0.00001
$C_{16}H_{34}O$	1-Hexadecanol	1	0	1	1	15	0	15	0	0	0	0	0	203.61343	203.603	-0.00005

Table 15.62. The bond angle parameters of alkyl alcohols and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle C_aOH$ (C_a-O (i))	2.67935	1.83616	3.6697	-14.82575	1	-14.82575	1	1	0.91771	0.75	1	0.75	0.91771	0				107.24	108.53 (methanol)
$\angle C_aOH$ (C_a-O (ii))	2.67024	1.83616	3.6515	-14.82575	1	-14.82575	1	1	0.91771	0.75	1	0.75	0.91771	0				106.78	105 (ethanol)
$\angle C_bC_aO$ (C_a-O (ii))	2.91547	2.67024	4.5826	-16.68412	25	-13.61806	O	0.81549	0.85395 (Eq (15.114))	1	1	1	0.83472	-1.65376				110.17	107.8 (ethanol)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

ETHERS ($C_nH_{2n+2}O_m$, $n = 2,3,4,5...\infty$)

The alkyl ethers, $C_nH_{2n+2}O_m$, comprise two types of $C-O$ functional groups, one for methyl or t-butyl groups corresponding to the C and the other for general alkyl groups. The alkyl portion of the alkyl ether may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in ethers are equivalent to those in branched-chain alkanes.

Each $C-O$ group is solved by hybridizing the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the O AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl ethers, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) and an energy of $E(C,2sp^3) = -14.63489\ eV$ (Eq. (15.25)) and the O AO has an energy of $E(O) = -13.61806\ eV$. To meet the equipotential condition of the union of the $C-O$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the $C-O$-bond MO given by Eq. (15.113) is $c_2(C2sp^3HO\ to\ O) = 0.85395$. $E_T(atom-atom,msp^3.AO)$ of the $C-O$-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is $-1.44915\ eV$ for the CH_3-O- and $(CH_3)_3C-O-$ $C-O$ groups. It is based on the energy match between the O AO, initially at the Coulomb potential of a proton and an electron (Eqs. (1.236) and (10.162), respectively), and the $C2sp^3$ HO of a methyl group as given by Eq. (14.151). For the alkyl $C-O$ group, $E_T(atom-atom,msp^3.AO)$ is $-1.65376\ eV$. It is based on the energy match between the O AO and the $C2sp^3$ HO of a methylene group and is given by the linear combination of $-0.72457\ eV$ (Eq. (14.151)) and $-0.92918\ eV$ (Eq. (14.513)), respectively.

The symbols of the functional groups of branched-chain alkyl ethers are given in Table 15.63. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl ethers are given in Tables 15.64, 15.65, and 15.66, respectively. The total energy of each alkyl ether given in Table 15.67 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.66 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl ethers determined using Eqs. (15.79-15.108) are given in Table 15.68.

Table 15.63. The symbols of functional groups of alkyl ethers.

Functional Group	Group Symbol
C-O (CH_3-O- and $(CH_3)_3C-O-$)	$C-O$ (i)
C-O (alkyl)	$C-O$ (ii)
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.64. The geometrical bond parameters of alkyl ethers and experimental values [1].

Parameter	$C-O$ (i) Group	$C-O$ (ii) Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.80717	1.79473	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.34431	1.33968	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ (Å)	1.42276	1.41785	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.416 (dimethyl ether)	1.418 (ethyl methyl ether (avg.))	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	1.20776	1.19429	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.74388	0.74645	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.65. The MO to HO intercept geometrical bond parameters of alkyl ethers. R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C-H\ (OC_aH_3)$	C_a	-0.72457	0	0	0	-152.34026	0.91771	0.87495	-15.55033	-15.35946	78.85	101.15	42.40	1.21777	0.16921
$H_3C_a-O-C_aH_3$ $(CH_3)_3C_a-O-C_bH_3$ $(CH_3)_3C_a-O-C_a(CH_3)_3$ $(C-O$ (i))	$C_{a,b}$	-0.72457	0	0	0	-152.34026	0.91771	0.87495	-15.55033	-15.35946	95.98	84.02	46.10	1.25319	0.09112
$H_3C_a-O-C_aH_3$ $(CH_3)_3C_a-O-C_bH_3$ $(CH_3)_3C_a-O-C_a(CH_3)_3$ $(C-O$ (i))	O	-0.72457	-0.72457	0	0		1.00000	0.83600	-16.27490		92.66	87.34	43.74	1.30555	0.03876
$-H_2C_a-OC_b(CH_3)_3$ $-H_2C_a-OC_bH_3$ $(C-O$ (ii))	C_a	-0.82688	-0.92918	0	0	-153.37175	0.91771	0.82053	-16.58181	-16.39095	92.41	87.59	43.35	1.30512	0.03456
$-H_2C_a-OC_b(CH_3)_3$ $-H_2C_a-OC_bH_3$ $(C-O$ (ii))	O	-0.72457	-0.82688	0	0		1.00000	0.83078	-16.37720		93.33	86.67	43.98	1.29138	0.04829
$-H_2C_a-O-H_2C_a-$ $(C-O$ (ii))	O	-0.82688	-0.82688	0	0		1.00000	0.82562	-16.47951		92.87	87.13	43.66	1.29829	0.04138
$C-H\ (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\ (CH)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.66. The energy parameters (eV) of functional groups of alkyl ethers.

Parameters	$C-O$ (i) Group	$C-O$ (ii) Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1
c_2	0.85395	0.85395	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	0	1	1	0	0	0	1	1	0
c_4	2	2	1	1	1	2	2	2	2	2	2
c_5	0	0	3	2	1	0	0	0	0	0	0
C_{1o}	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	1	1	1	1	1	1	1	1	1	1	1
V_e (eV)	-33.15757	-33.47304	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	10.12103	10.15605	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	9.17389	9.32537	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_m (eV)	-4.58695	-4.66268	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(AO/HO)$ (eV)	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(AO/HO)$ (eV)	-1.44915	-1.65376	0	0	0	0	0	0	0	0	0
$E_T(AO/HO)$ (eV)	-13.18574	-12.98113	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(H_2MO)$ (eV)	-31.63533	-31.63544	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom, msp^3.AO)$ (eV)	-1.44915	-1.65376	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(MO)$ (eV)	-33.08452	-33.28912	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω $(10^{15}\ rad/s)$	12.0329	12.1583	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	7.92028	8.00277	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D$ (eV)	-0.18420	-0.18631	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}$ (eV)	0.13663 [21]	0.16118 [4]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}$ (eV)	-0.11589	-0.10572	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mag} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(Group)$ (eV)	-33.20040	-33.39484	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(c_4\ AO/HO)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(c_5\ AO/HO)$ (eV)	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(Group)$ (eV)	3.93062	4.12506	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.67. The total bond energies of alkyl ethers calculated using the functional group composition and the energies of Table 15.66 compared to the experimental values [3].

Formula	Name	$C-O$ (i) Group	$C-O$ (ii) Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_6O	Dimethyl ether	2	0	2	0	0	0	0	0	0	0	0	32.84496	32.902	0.00174
C_3H_8O	Ethyl methyl ether	1	1	2	1	0	1	0	0	0	0	0	45.19710	45.183	-0.00030
$C_4H_{10}O$	Diethyl ether	0	2	2	2	0	2	0	0	0	0	0	57.54924	57.500	-0.00086
$C_4H_{10}O$	Methyl propyl ether	1	1	2	2	0	2	0	0	0	0	0	57.35480	57.355	0.00000
$C_4H_{10}O$	Isopropyl methyl ether	1	1	3	0	1	0	2	0	0	0	0	57.45569	57.499	0.00075
$C_6H_{14}O$	Dipropyl ether	0	2	2	4	0	4	0	0	0	0	0	81.86464	81.817	-0.00059
$C_6H_{14}O$	Diisopropyl ether	0	2	4	0	2	0	4	0	0	0	0	82.06642	82.088	0.00026
$C_6H_{14}O$	t-Butyl ethyl ether	1	1	4	1	0	1	0	3	0	0	0	82.10276	82.033	-0.00085
$C_7H_{16}O$	t-Butyl isopropyl ether	1	1	5	0	1	0	2	3	0	0	0	94.36135	94.438	0.00081
$C_8H_{18}O$	Dibutyl ether	0	2	2	6	0	6	0	0	0	0	0	106.18004	106.122	-0.00055
$C_8H_{18}O$	Di-sec-butyl ether	0	2	4	2	2	2	4	0	0	0	0	106.38182	106.410	0.00027
$C_8H_{18}O$	Di-t-butyl ether	2	0	6	0	0	0	0	6	0	0	0	106.65628	106.425	-0.00218
$C_8H_{18}O$	t-Butyl isobutyl ether	1	1	5	1	1	0	3	3	0	0	0	106.49072	106.497	0.00006

Table 15.68. The bond angle parameters of alkyl ethers and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom, msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle C_aOC_a$ (C_a-O (i))	2.68862	2.68862	4.4721	-17.40869	38	-17.40869	38	0.78155	0.78155	1	1	1	0.78155	-1.85836				112.54	112 (dimethyl ether)
$\angle C_aOC_b$ (C_a-O (i)) (C_b-O (ii))	2.68862	2.67935	4.4385	-17.51099	41	-17.51099	41	0.77699	0.77699	1	1	1	0.77699	-1.85836				111.55	111.9 (ethyl methyl ether)
$\angle C_bC_aO$ (C_a-O (ii))	2.91547	2.67935	4.5607	-16.68412	25	-13.61806	O	0.81549	0.85395 (Eq. (15.114))	1	1	1	0.83472	-1.65376				109.13	109.4 (ethyl methyl ether)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

PRIMARY AMINES ($C_nH_{2n+2+m}N_m$, $n = 1,2,3,4,5...\infty$)

The primary amines, $C_nH_{2n+2+m}N_m$, comprise an NH_2 functional group and a $C-N$ functional group. The alkyl portion of the primary amine may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in primary amines are equivalent to those in branched-chain alkanes.

The primary amino (NH_2) functional group was solved using the procedure given in the Dihydrogen Nitride (NH_2) section. Using the results of Eqs. (13.245-13.368), the primary amino parameters in Eq. (15.52) are $n_1 = 2$, $C_1 = 0.75$, $C_2 = 0.93613$ (Eqs. (13.248-13.249)), $C_{1o} = 1.5$, and $c_1 = 0.75$. In primary amines, the $C2sp^3$ HO of the $C-NH_2$-bond MO has an energy of $E(C,2sp^3) = -15.35946\ eV$ (Eq. (15.18) with $s=1$ and Eqs. (15.19-15.20)) and the N AO has an energy of $E(N) = -14.53414\ eV$. To meet the equipotential condition of the union of the $N-H$ H_2-type-ellipsoidal-MO with the $C2sp^3$ HO, the hybridization factor c_2 of Eq. (15.52) for the $N-H$-bond MO given by Eq. (15.68) is

$$c_2(H\ to\ 1°N) = \frac{E(N)}{E(C,2sp^3)} = \frac{-14.53414\ eV}{-15.35946\ eV} = 0.94627 \tag{15.115}$$

The $C-N$ group is solved by hybridizing the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the N AO to form a MO permits each participating orbital to decrease in radius and energy. In primary amines, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3) = -14.63489\ eV$ (Eq. (15.25)), and the N AO has an energy of $E(N) = -14.53414\ eV$. To meet the equipotential condition of the union of the

$C-N$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the $C-N$-bond MO given by Eqs. (15.68) and (15.70) is

$$c_2(C2sp^3HO\ to\ N)=\frac{E(N)}{E(C,2sp^3)}c_2(C2sp^3HO)=\frac{-14.53414\ eV}{-14.63489\ eV}(0.91771)=0.91140 \quad (15.116)$$

$E_T(atom-atom,msp^3.AO)$ of the $C-N$-bond MO in Eq. (15.52) due to the charge donation from the C and N atoms to the MO is $-1.44915\ eV$. It is based on the energy match between the N of the NH_2 group and the $C2sp^3$. HO corresponding to the energy contributions to the single bond that are equivalent to those of methyl groups, $-0.72457\ eV$ (Eq. (14.151)), where the $N-H$ bonds are also energy matched to the $C-N$ bond.

The symbols of the functional groups of branched-chain primary amines are given in Table 15.69. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of primary amines are given in Tables 15.70, 15.71, and 15.72, respectively. The total energy of each primary amine given in Table 15.73 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.72 corresponding to functional-group composition of the molecule. The bond angle parameters of primary amines determined using Eqs. (15.79-15.108) are given in Table 15.74.

Table 15.69. The symbols of functional groups of primary amines.

Functional Group	Group Symbol
NH_2 group	NH_2
C-N	$C-N$
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.70. The geometrical bond parameters of primary amines and experimental values [1].

Parameter	NH_2 Group	$C-N$ Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.28083	1.92682	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	0.95506	1.38810	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ (Å)	1.0108	1.46910	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.010 (methylamine)	1.471 (methylamine)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	0.85345	1.33634	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.74566	0.72041	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.71. The MO to HO intercept geometrical bond parameters of primary amines. R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$H_3CN(H)-H$	N	-0.72457	0	0	0		0.93084	0.87495	-15.55033		118.00	62.00	64.85	0.54432	0.41075
$-H_2C_aN(H)-H$	N	-0.72457	0	0	0		0.93084	0.87495	-15.55033		118.00	62.00	64.85	0.54432	0.41075
H_3C-NH_2	C	-0.72457	0	0	0	-152.34026	0.91771	0.87495	-15.55033	-15.35946	85.28	94.72	40.73	1.46010	0.07200
H_3C-NH_2	N	-0.72457	0	0	0		0.93084	0.87495	-15.55033		85.28	94.72	40.73	1.46010	0.07200
$-H_2C_a-NH_2$	C_a	-0.72457	-0.92918	0	0	-153.26945	0.91771	0.82562	-16.47951	-16.28864	80.20	99.80	37.50	1.52858	0.14048
$-H_2C_a-NH_2$	N	-0.72457	0	0	0		0.93084	0.87495	-15.55033		85.28	94.72	40.73	1.46010	0.07200
$C-H\ (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\ (CH)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ ($C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ ($C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.72. The energy parameters (eV) of functional groups of primary amines.

Parameters	NH_2 Group	$C-N$ Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	2	1	3	2	1	1	1	1	1	1	1
n_2	0	0	2	1	0	0	0	0	0	0	0
n_3	1	0	0	0	0	0	0	0	0	0	0
C_1	0.75	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	0.93613	1	1	1	1	1	1	1	1	1	1
c_1	0.75	1	1	1	1	1	1	1	1	1	1
c_2	0.94627	0.91140	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	0	1	1	0	0	0	1	1	0
c_4	1	2	1	1	1	2	2	2	2	2	2
c_5	2	0	3	2	1	0	0	0	0	0	0
C_{1o}	1.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	1	1	1	1	1	1	1	1	1	1	1
$V_e\ (eV)$	-77.89897	-32.46339	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_p\ (eV)$	28.49191	9.80175	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
$T\ (eV)$	30.40957	8.42409	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$V_m\ (eV)$	-15.20478	-4.21204	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(AO/HO)\ (eV)$	-14.53414	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(AO/HO)\ (eV)$	0	-1.44915	0	0	0	0	0	0	0	0	0
$E_T(AO/HO)\ (eV)$	-14.53414	-13.18574	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E(n_3\ AO/HO)\ (eV)$	-14.53414	0	0	0	0	0	0	0	0	0	0
$E_T(H_2MO)\ (eV)$	-48.73642	-31.63534	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom,msp^3.AO)\ (eV)$	0	-1.44915	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(MO)\ (eV)$	-48.73660	-33.08452	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\ (10^{15}\ rad/s)$	64.2189	18.9231	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_K\ (eV)$	42.27003	12.45552	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D\ (eV)$	-0.40690	-0.23100	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}\ (eV)$	0.40929 [22]	0.12944 [23]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}\ (eV)$	-0.20226	-0.16628	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{mag}\ (eV)$	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(Group)\ (eV)$	-49.14112	-33.25079	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(c_4\ AO/HO)\ (eV)$	-14.53414	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(c_5\ AO/HO)\ (eV)$	-13.59844	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(Group)\ (eV)$	7.41010	3.98101	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.73. The total bond energies of primary amines calculated using the functional group composition and the energies of Table 15.72 compared to the experimental values [3].

Formula	Name	NH_2 Group	$C-N$ Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_5N	Methylamine	1	1	1	0	0	0	0	0	0	0	0	23.88297	23.857	-0.00110
C_2H_7N	Ethylamine	1	1	1	1	0	1	0	0	0	0	0	36.04067	36.062	0.00060
C_3H_9N	Propylamine	1	1	1	2	0	2	0	0	0	0	0	48.19837	48.243	0.00092
$C_4H_{11}N$	Butylamine	1	1	1	3	0	3	0	0	0	0	0	60.35607	60.415	0.00098
$C_4H_{11}N$	sec-Butylamine	1	1	2	1	1	1	2	0	0	0	0	60.45696	60.547	0.00148
$C_4H_{11}N$	t-Butylamine	1	1	3	0	0	0	0	3	0	0	0	60.78863	60.717	-0.00118
$C_4H_{11}N$	Isobutylamine	1	1	2	1	1	0	3	0	0	0	0	60.42863	60.486	0.00094

Table 15.74. The bond angle parameters of primary amines and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ or E Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HNH$	1.91013	1.91013	3.0984	-14.53414	N	H	H	0.94627 Eq. (15.115))	1	1	1	0.75	1.05679	0				108.40	107.1 (methylamine)
$\angle HNC'_a$	1.91013	2.77620	3.8816	-14.53414	5	-15.35946	N	0.91140 (Eq. (15.116))	0.88583	0.75	1	0.75	0.97194	0				110.48	110.3 (methylamine)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	108.0 (methylamine) 107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC'_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C'_aC'_bC'_c$															70.56			109.44	
$\angle C'_aC'_bH$															70.56			109.44	
$\angle C'_bC'_aC'_c$ iso C'_a	2.91547	2.91547	4.7958	-16.68412 C'_b	25	-16.68412 C'_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C'_bC'_aH$ iso C'_a	2.91547	2.11323	4.1633	-15.55033 C'_a	5	-14.82575 C'_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C'_aC'_bH$ iso C'_a	2.91547	2.09711	4.1633	-15.55033 C'_b	5	-14.82575 C'_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C'_bC'_aC'_c$ tert C'_a	2.90327	2.90327	4.7958	-15.55033 C'_b	5	-14.82575 C'_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C'_bC'_aC'_d$															72.50			107.50	

SECONDARY AMINES ($C_nH_{2n+2+m}N_m$, $n = 2,3,4,5...\infty$)

The secondary amines, $C_nH_{2n+2+m}N_m$, comprise an NH functional group and two types of $C-N$ functional groups, one for the methyl group corresponding to the C of $C-N$ and the other for general alkyl secondary amines. The alkyl portion of the secondary amine may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in secondary amines are equivalent to those in branched-chain alkanes.

The secondary amino (NH) functional group was solved using the procedure given in the Hydrogen Nitride (NH) section. Using the results of Eqs. (13.245-13.316), the secondary amino parameters in Eq. (15.52) are $n_1 = 1$, $C_1 = 0.75$, $C_2 = 0.93613$ (Eqs. (13.248-13.249)), $C_{1o} = 0.75$, and $c_1 = 0.75$. In secondary amines, the $C2sp^3$ HO of the $C-NH$-bond MO has an energy of $E(C,2sp^3) = -15.56407\ eV$ (Eqs. (14.514-14.516)); Eq. (15.29) with $s=1$ and $s=2$, Eq. (15.31), and Eqs. (15.19-15.20)) and the N AO has an energy of $E(N) = -14.53414\ eV$. To meet the equipotential condition of the union of the $N-H$ H_2-type-ellipsoidal-MO with the $C2sp^3$ HO, the hybridization factor c_2 of Eq. (15.52) for the $N-H$-bond MO given by Eq. (15.68) is

$$c_2(H\ to\ 2°N) = \frac{E(N)}{E(C,2sp^3)} = \frac{-14.53414\ eV}{-15.56407\ eV} = 0.93383 \tag{15.117}$$

The $C-N$ group is solved by hybridizing the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the N AO to form a MO permits each participating orbital to decrease in radius and energy. In secondary amines, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3) = -14.63489\ eV$ (Eq. (15.25)), and the N AO has an energy of $E(N) = -14.53414\ eV$. To meet the equipotential condition of the union of the

$C-N$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the $C-N$-bond MO given by Eq. (15.116) is $c_2\left(C2sp^3HO\ to\ N\right)=0.91140$.

As given in the Continuous-Chain Alkanes (C_nH_{2n+2}, $n=3,4,5...\infty$) section, each methylene group forms two single bonds, and the energy of each $C2sp^3$ HO of each CH_2 group alone is given by that in ethylene, $-1.13379\ eV$ (Eq. (14.511)). In secondary amines, the N of the NH group also binds to two $C2sp^3$ HOs and the corresponding $E_T\left(atom-atom,msp^3.AO\right)$ of each $C-N$-bond MO in Eq. (15.52) due to the charge donation from the C and N atoms to the MO is $-1.13379\ eV$. It is based on the energy match between the N of the NH group to the two $C2sp^3$ HOs corresponding to the energy contributions to each of the two single bonds that are equivalent to those of independent methylene groups, $-1.13379\ eV$ (Eq. (14.511)), where the $N-H$ bond is also energy matched to the $C-N$ bonds. $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-N$-bond MO in Eq. (15.52) due to the charge donation from the C and N atoms to the MO is $-1.13379\ eV$. It is based on the energy match between the N of the NH group to two $C2sp^3$ HOs corresponding to the energy contributions to the single bond that are equivalent to those of methyl groups, $-0.72457\ eV$ (Eq. (14.151)), where the $N-H$ bonds are also energy matched to the $C-N$ bond.

The symbols of the functional groups of branched-chain secondary amines are given in Table 15.75. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of secondary amines are given in Tables 15.76, 15.77, and 15.78, respectively. As in the case of NH_2 (Eq. (13.339)), $C_{1o}=2C_1$ rather than $C_{1o}=C_1$ in Eq. (15.52) for the $C-N$ bond. The total energy of each secondary amine given in Table 15.79 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.78 corresponding to functional-group composition of the molecule. The bond angle parameters of secondary amines determined using Eqs. (15.79-15.108) are given in Table 15.80.

Table 15.75. The symbols of functional groups of secondary amines.

Functional Group	Group Symbol
NH group	NH
C-N (methyl)	$C-N$ (i)
C-N (alkyl)	$C-N$ (ii)
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.76. The geometrical bond parameters of secondary amines and experimental values [1].

Parameter	NH Group	$C-N$ (i) Group	$C-N$ (ii) Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.26224	1.94862	1.94862	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	0.94811	1.39593	1.39593	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ ($\mathring{A}$)	1.00343	1.47739	1.47739	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length ($\mathring{A}$)	1.00 (dimethylamine)	1.455 (dimethylamine)		1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b, c\ (a_0)$	0.83327	1.35960	1.35960	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.75113	0.71637	0.71637	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.77. The MO to HO intercept geometrical bond parameters of secondary amines. R, R', R'' are H or alkyl groups. E_T is $E_T(atom-atom, msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$H_3C_aN(C_bH_3)-H$	N	-0.56690	-0.56690	0	0		0.93084	0.85252	-15.95954		118.18	61.82	64.40	0.54546	0.40264
$-H_2C_aN(R_{alkyl})-H$	N	-0.56690	-0.56690	0	0		0.93084	0.85252	-15.95954		118.18	61.82	64.40	0.54546	0.40264
$H_3C_a-NH-C_aH_3$	C_a	-0.56690	0	0	0	-152.18259	0.91771	0.88392	-15.39265	-15.20178	84.14	95.86	40.30	1.48625	0.09032
$H_3C_a-NH-C_aH_3$	N	-0.56690	-0.56690	0	0		0.93084	0.85252	-15.95954		80.95	99.05	38.26	1.53008	0.13415
$-H_2C_a-NH-C_bR$	C_a	-0.56690	-0.92918	0	0	-153.11177	0.91771	0.83360	-16.32183	-16.13097	78.89	101.11	36.99	1.55650	0.16057
$-H_2C_a-NH-C_bH_2-$	N	-0.56690	-0.56690	0	0		0.93084	0.85252	-15.95954		80.95	99.05	38.26	1.53008	0.13415
$C-H\ (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\ (CH)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a)$)$	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a)$)$	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (b)$)$	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (c)$)$	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (d)$)$	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (e)$)$	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (f)$)$	C_b	-0.72457	-0.92918	-0.92918	0	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (f)$)$	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.78. The energy parameters (eV) of functional groups of secondary amines.

Parameters	NH Group	$C-N$ (i) Group	$C-N$ (ii) Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.75	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	0.93613	1	1	1	1	1	1	1	1	1	1	1
c_1	0.75	1	1	1	1	1	1	1	1	1	1	1
c_2	0.93383	0.91140	0.91140	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	1	0	0	0	1	1	0	0	0	1	1	0
c_4	1	2	2	1	1	1	2	2	2	2	2	2
c_5	1	0	0	3	2	1	0	0	0	0	0	0
C_{1o}	0.75	1	1	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	1	1	1	1	1	1	1	1	1	1	1	1
V_e (eV)	-39.21967	-31.98456	-31.98456	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	14.35050	9.74677	9.74677	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	15.53581	8.20698	8.20698	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_m (eV)	-7.76790	-4.10349	-4.10349	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(_{AO/HO})$ (eV)	-14.53414	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(_{AO/HO})$ (eV)	0	-1.13379	-1.13379	0	0	0	0	0	0	0	0	0
$E_T(_{AO/HO})$ (eV)	-14.53414	-13.50110	-13.50110	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(_{H_2MO})$ (eV)	-31.63541	-31.63540	-31.63540	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T\left(atom-atom,msp^3.AO\right)$ (eV)	0	-1.13379	-1.13379	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(_{MO})$ (eV)	-31.63537	-32.76916	-32.76916	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω $\left(10^{15}\ rad/s\right)$	47.0696	15.1983	26.0778	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	30.98202	10.00377	17.16484	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D$ (eV)	-0.34836	-0.20505	-0.26859	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}$ (eV)	0.40696 [24]	0.12944 [23]	0.11159 [25]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}$ (eV)	-0.14488	-0.14033	-0.21280	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mag} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(_{Group})$ (eV)	-31.78025	-32.90949	-32.98196	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(_{c_4\ AO/HO})$ (eV)	-14.53414	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(_{c_5\ AO/HO})$ (eV)	-13.59844	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(_{Group})$ (eV)	3.50582	3.63971	3.71218	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.79. The total bond energies of secondary amines calculated using the functional group composition and the energies of Table 15.78 compared to the experimental values [3].

Formula	Name	NH Group	$C-N$ (i) Group	$C-N$ (ii) Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_7N	Dimethylamine	1	2	0	2	0	0	0	0	0	0	0	0	35.76895	35.765	-0.00012
$C_4H_{11}N$	Diethylamine	1	0	2	2	2	0	2	0	0	0	0	0	60.22930	60.211	-0.00030
$C_6H_{15}N$	Dipropylamine	1	0	2	2	4	0	4	0	0	0	0	0	84.54470	84.558	0.00016
$C_6H_{15}N$	Diisopropylamine	1	0	2	4	0	2	0	4	0	0	0	0	84.74648	84.846	0.00117
$C_8H_{19}N$	Dibutylamine	1	0	2	2	6	0	6	0	0	0	0	0	108.86010	108.872	0.00011
$C_8H_{19}N$	Diisobutylamine	1	0	2	4	2	2	0	6	0	0	0	0	109.00522	109.106	0.00092

Table 15.80. The bond angle parameters of secondary amines and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom, msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ or E Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HCN$ $(C-N$ (i) & (ii))	2.09711	2.79186	4.0661	-14.82575	N	-14.53414	1	0.91771	0.93383 Eq. (15.117))	0.75	1	0.75	1.01756	0				111.76	112 (dimethylamine)
$\angle HNC_a$ $(C-N$ (i) & (ii))	1.89621	2.79186	3.8123	-14.53414	7	-15.56407 (Eq. (15.117))	N	0.91140 (Eq. (15.116))	0.87418	0.75	1	0.75	0.95917	0				107.27	107 (dimethylamine)
$\angle CNC$ $(C-N$ (i) & (ii))	2.79186	2.79186	4.6260	-17.04640	29	-17.04640	29	0.79816	0.79816	1	1	1	0.79816	-1.85836				111.89	111.8 (dimethylamine)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (dimethylamine) 107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$																			
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836	70.56			109.44 110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

TERTIARY AMINES ($C_nH_{2n+3}N,\ n=3,4,5...\infty$)

The tertiary amines, $C_nH_{2n+3}N$, have three $C-N$ bonds to methyl or alkyl groups wherein $C-N$ comprises a functional group. The alkyl portion of the tertiary amine may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in tertiary amines are equivalent to those in branched-chain alkanes.

The $C-N$ group is solved by hybridizing the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the N AO to form a MO permits each participating orbital to decrease in radius and energy. In tertiary amines, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3)=-14.63489\ eV$ (Eq. (15.25)), and the N AO has an energy of $E(N)=-14.53414\ eV$. To meet the equipotential condition of the union of the $C-N$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the $C-N$-bond MO given by Eq. (15.116) is $c_2(C2sp^3HO\ to\ \mathrm{N})=0.91140$.

As given in the Continuous-Chain Alkanes ($C_nH_{2n+2},\ n=3,4,5...\infty$) section, the energy of each $C2sp^3$ HO must be a linear combination of that of the CH_3 and CH_2 groups that serve as basis elements. Each CH_3 forms one $C-C$ bond, and each CH_2 group forms two. Thus, the energy of each $C2sp^3$ HO of each CH_3 and CH_2 group alone is given by that in ethane, $-0.72457\ eV$ (Eq. (14.151)), and ethylene, $-1.13379\ eV$ (Eq. (14.511)), respectively. In order to match the energy of the component HOs and MOs for the entire molecule, the energy $E_{T_{alkane}}(C-C,2sp^3)$ given as a linear combination of these basis elements is $-0.92918\ eV$ (Eq. (14.513)). In tertiary amines, the N binds to three $C2sp^3$ HOs and the corresponding $E_T(atom-atom,msp^3.AO)$ of each $C-N$-bond MO in Eq. (15.52) due to the charge donation

from the C and N atoms to the MO is $-0.92918\ eV$. It comprises a linear combination of the energy for a primary amine, $-0.72457\ eV$ and a secondary amine, $-1.13379\ eV$.

The symbols of the functional groups of branched-chain tertiary amines are given in Table 15.81. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of tertiary amines are given in Tables 15.82, 15.83, and 15.84, respectively. The total energy of each tertiary amine given in Table 15.85 was calculated as the sum over the integer multiple of each $E_D(_{Group})$ of Table 15.84 corresponding to functional-group composition of the molecule. The bond angle parameters of tertiary amines determined using Eqs. (15.79-15.108) are given in Table 15.86.

Table 15.81. The symbols of functional groups of tertiary amines.

Functional Group	Group Symbol
C-N	$C-N$
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.82. The geometrical bond parameters of tertiary amines and experimental values [1].

Parameter	$C-N$ Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.96313	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.40112	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (Å)$	1.48288	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(Å)$	1.458 (trimethylamine)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	1.37505	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.71372	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.83. The MO to HO intercept geometrical bond parameters of tertiary amines. R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' $(^\circ)$	θ_1 $(^\circ)$	θ_2 $(^\circ)$	d_1 (a_0)	d_2 (a_0)
$N-(C_aH_3)_3$	C_a	-0.46459		0	0	-152.08028	0.91771	0.88983	-15.29034	-15.09948	83.37	96.63	40.00	1.50383	0.10271
$N-(C_aH_3)_3$	N	-0.46459	-0.46459	-0.46459	0		0.93084	0.83885	-16.21953		78.02	101.98	36.64	1.57525	0.17413
$N-(C_aH_2-)_3$	C_a	-0.46459	-0.92918	0	0	-153.00946	0.91771	0.83885	-16.21953	-16.02866	78.02	101.98	36.64	1.57525	0.17413
$N-(C_aH_2-)_3$	N	-0.46459	-0.46459	-0.46459	0		0.93084	0.83885	-16.21953		78.02	101.98	36.64	1.57525	0.17413
$C-H\ (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\ (CH)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ $(C-C\ \text{(a)})$	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ $(C-C\ \text{(a)})$	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b(H_2C_c-R')HCH_2-$ $(C-C\ \text{(b)})$	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C\ \text{(c)})$	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b(H_2C_c-R')HCH_2-$ $(C-C\ \text{(d)})$	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C\ \text{(e)})$	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b(H_2C_c-R')HCH_2-$ $(C-C\ \text{(f)})$	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C\ \text{(f)})$	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.84. The energy parameters (eV) of functional groups of tertiary amines.

Parameters	$C-N$ Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	3	2	1	1	1	1	1	1	1
n_2	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1
c_2	0.91140	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	1	1	0	0	0	1	1	0
c_4	2	1	1	1	2	2	2	2	2	2
c_5	0	3	2	1	0	0	0	0	0	0
C_{1o}	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	1	1	1	1	1	1	1	1	1	1
$V_e\ (eV)$	-31.67393	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_p\ (eV)$	9.71067	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
$T\ (eV)$	8.06719	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$V_m\ (eV)$	-4.03359	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(AO/HO)\ (eV)$	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(AO/HO)\ (eV)$	-0.92918	0	0	0	0	0	0	0	0	0
$E_T(AO/HO)\ (eV)$	-13.70571	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(H_2MO)\ (eV)$	-31.63537	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom,msp^3.AO)\ (eV)$	-0.92918	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(MO)\ (eV)$	-32.56455	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\ (10^{15}\ rad/s)$	18.1298	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_K\ (eV)$	11.93333	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D\ (eV)$	-0.22255	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}\ (eV)$	0.12944 [23]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}\ (eV)$	-0.15783	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{mag}\ (eV)$	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(Group)\ (eV)$	-32.72238	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(c_4\ AO/HO)\ (eV)$	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(c_5\ AO/HO)\ (eV)$	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(Group)\ (eV)$	3.45260	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.85. The total bond energies of tertiary amines calculated using the functional group composition and the energies of Table 15.84 compared to the experimental values [3].

Formula	Name	$C-N$ Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_3H_9N	Trimethylamine	3	3	0	0	0	0	0	0	0	0	47.83338	47.761	-0.00152
$C_6H_{15}N$	Triethylamine	3	3	3	0	3	0	0	0	0	0	84.30648	84.316	0.00012
$C_9H_{21}N$	Tripropylamine	3	3	6	0	6	0	0	0	0	0	120.77958	120.864	0.00070

Table 15.86. The bond angle parameters of tertiary amines and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ or E Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	$\bar{c}_1$	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CNC$	2.80224	2.80224	4.6043	-17.14871	1	-17.14871	6	0.79340	0.79340	1	1	1	0.79340	-1.85836				110.48	110.9 (trimethylamine)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (dimethylamine) 107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$																			
$\angle C_aC_bH$															70.56			109.44	
															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

ALDEHYDES ($C_nH_{2n}O,\ n=1,2,3,4,5...\infty$)

The alkyl aldehydes, $C_nH_{2n}O$, each have a $HC=O$ moiety that comprises a $C=O$ functional group and a CH functional group. The single bond of carbon to the carbonyl carbon atom, $C-C(O)H$, is a functional group. In addition to the $C=O$ functional group, formaldehyde comprises a CH_2 functional group. The alkyl portion of the alkyl aldehyde may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in aldehydes are equivalent to those in branched-chain alkanes.

The CH functional group was solved in the Hydrogen Carbide (CH) section except that E_{mag} is not subtracted since unpaired electrons are not created with fragmentation of the CH functional group of aldehydes. The CH_2 functional group of formaldehyde is solved in the Dihydrogen Carbide (CH_2) section except that the energy of each $C-H$ MO is matched to the initial energy of the $C2sp^3$ HO (Eq. (15.25)). The $C=O$ and $C-C(O)H$ groups are solved by hybridizing the $2s$ and $2p$ AOs of each C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the O AO or between two $C2sp^3$ HOs, respectively, to form a MO permits each participating orbital to decrease in radius and energy. In alkyl aldehydes, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3)=-14.63489\ eV$ (Eq. (15.25)) and the O AO has an energy of $E(O)=-13.61806\ eV$. To meet the equipotential condition of the union of the $C=O$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the $C=O$-bond MO given by Eq. (15.114) is $c_2(C2sp^3HO\ to\ O)=0.85395$. The unpaired electrons created by bond breakage of the double $C=O$ bond requires that two times

the $O2p$ AO magnetic energy E_{mag} (Eq. (15.60)) be subtracted from the total energy to give $E_D(Group)$ (eV) for $C=O$.

$E_T\left(atom-atom,msp^3.AO\right)$ of the $C=O$-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is $-2.69893\ eV$ which is an energy minimum for the double bond between the pair of $C2sp^3$ HO electrons of the C atom and the pair of AO electrons of the O atom. It is given as a linear combination of the energy contributions corresponding to a double bond, $-1.13379\ eV$ (Eq. (14.247)), and a triple bond, $-1.56513\ eV$ (Eq. (14.342)). The triple bond contribution includes the $C2sp^3$ HO electron of the $C-H$ bond in addition to the pair involved directly in the double bond with O. $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-C(O)H$ group is equivalent to that of an alkane, $-1.85836\ eV$, where both energy contributions are given by Eq. (14.513). It is based on the energy match between the $C2sp^3$ HOs of the aldehyde. In order to match energy between the groups bonded to the $C=O$, electron-density is shared. Due to the interaction in the transition state between the groups based on the sharing, $C_{1o}=2C_1$ rather than $C_{1o}=C_1$ in Eq. (15.52) for the $C-C(O)H$ bond.

The symbols of the functional groups of alkyl aldehydes are given in Table 15.87. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl aldehydes are given in Tables 15.88, 15.89, and 15.90, respectively. The total energy of each alkyl aldehyde given in Table 15.91 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.90 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl aldehydes determined using Eqs. (15.79-15.108) are given in Table 15.92.

Table 15.87. The symbols of functional groups of alkyl aldehydes.

Functional Group	Group Symbol
CH_2 (formaldehyde) group	$C-H\ (CH_2)$ (i)
CH (aldehyde) group	CH (i)
C=O	$C=O$ (i)
C-C(O)H	$C-C(O)H$
CH_3 group	$C-H\ (CH_3)$
CH_2 (alkyl) group	$C-H\ (CH_2)$ (ii)
CH (alkyl)	$C-H$ (ii)
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.88. The geometrical bond parameters of alkyl aldehydes and experimental values [1].

Parameter	$C'-H\ (CH_2)$ (i)	CH (i) Group	$C=O$ Group	$C-C(O)H$ Group	$C'-H\ (CH_3)$ Group	$C-H\ (CH_2)$ (ii) Group	$C-H$ (ii) Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.64010	1.67465	1.29907	2.04740	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.04566	1.05661	1.13977	1.43087	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ (Å)	1.10668	1.11827	1.20628	1.51437	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.116 (formaldehyde)	1.128 (acetaldehyde)	1.208 (formaldehyde) 1.210 (acetaldehyde)	1.515 (acetaldehyde)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	1.26354	1.29924	0.62331	1.46439	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.63756	0.63095	0.87737	0.69887	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.89. The MO to HO intercept geometrical bond parameters of alkyl aldehydes. R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$HC(O)-H\ (CH_2)$ (i)	C'	-1.34946	0	0	0	-152.96515	0.91771	0.84115	-16.17521	-15.98435	75.72	104.28	40.18	1.25314	0.20748
$-C_bH_2C_a(O)-H\ (CH)$ (i)	C'_a	-1.34946	-0.92918	0	0	-153.89434	0.91771	0.79546	-17.10440	-16.91353	64.95	115.05	33.69	1.39345	0.33684
$H_2C=O$	O	-1.34946	0	0	0		1.00000	0.84115	-16.17521		137.27	42.73	66.31	0.52193	0.61784
$-C_bH_2C_a(H)=O$	O	-1.34946	0	0	0		1.00000	0.84115	-16.17521		137.27	42.73	66.31	0.52193	0.61784
$RH_2C_b-C_a(H)(O)$	C'_a	-1.34946	-0.92918	0	0	-153.89434	0.91771	0.79546	-17.10440	-16.91353	135.34	44.66	63.78	0.57401	0.56576
$H_3C_b-C_a(H)(O)$	C'_b	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	72.27	107.73	34.17	1.69388	0.26301
$-C_bH_2-C_a(H)(O)$	C'_b	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	65.99	114.01	30.58	1.76270	0.33183
$C'-H\ (CH_3)$	C'	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C'-H\ (CH_2)$ (ii)	C'	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C'-H\ (CH)$ (ii)	C'	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C'_aC'_bH_2CH_2-$ ($C'-C'$ (a))	C'_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C'_aC'_bH_2CH_2-$ ($C'-C'$ (a))	C'_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C'_aC_b(H_2C_c-R')HCH_2-$ ($C'-C'$ (b))	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C'_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C'-C'$ (c))	C'_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC'_aC'_b(H_2C_c-R')HCH_2-$ ($C'-C'$ (d))	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC'_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C'-C'$ (e))	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC'_aC_b(H_2C_c-R')HCH_2-$ ($C'-C'$ (f))	C'_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC'_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C'-C'$ (f))	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.90. The energy parameters (eV) of functional groups of alkyl aldehydes.

Parameters	CH_2 (i)	CH (i) Group	$C=O$ Group	$C-C(O)H$ Group	CH_3 Group	CH_2 (ii) Group	$C-H$ (ii) Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	2	1	2	1	3	2	1	1	1	1	1	1	1
n_2	1	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.75	0.75	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1	1	1
c_2	0.91771	0.91771	0.85395	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	1	0	2	0	0	1	1	0	0	0	1	1	0
c_4	1	1	4	2	1	1	1	2	2	2	2	2	2
c_5	2	1	0	0	3	2	1	0	0	0	0	0	0
C_{1o}	0.75	0.75	0.5	1	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	1	1	1	1	1	1	1	1	1	1	1	1	1
V_e (eV)	-72.03287	-35.12015	-111.25473	-30.19634	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	26.02344	12.87680	23.87467	9.50874	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	21.95990	10.48582	42.82081	7.37432	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_m (eV)	-10.97995	-5.24291	-21.41040	-3.68716	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(_{AO/HO})$ (eV)	-14.63489	-14.63489	0	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(_{AO/HO})$ (eV)	0	0	-2.69893	0	0	0	0	0	0	0	0	0	0
$E_T(_{AO/HO})$ (eV)	-14.63489	-14.63489	2.69893	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(_{H_2MO})$ (eV)	-49.66437	-31.63533	-63.27074	-31.63534	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom,msp^3.AO)$ (eV)	0	0	-2.69893	-1.85836	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(_{MO})$ (eV)	-49.66493	-31.63537	-65.96966	-33.49373	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω $(10^{15}$ $rad/s)$	25.2077	24.1759	59.4034	23.3291	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	16.59214	15.91299	39.10034	15.35563	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D$ (eV)	-0.25493	-0.24966	-0.40804	-0.25966	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}$ (eV)	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.21077 [12]	0.13800 [26]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}$ (eV)	-0.07727	-0.07200	-0.30266	-0.19066	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mag} (eV)	0.14803	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(_{Group})$ (eV)	-49.81948	-31.70737	-66.57498	-33.68439	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(_{c_4\ AO/HO})$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(_{c_5\ AO/HO})$ (eV)	-13.59844	-13.59844	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(_{Group})$ (eV)	7.83968	3.47404	7.80660	4.41461	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.91. The total bond energies of alkyl aldehydes calculated using the functional group composition and the energies of Table 15.90 compared to the experimental values [3].

Formula	Name	CH_2 (i) Group	CH (i) Group	$C=O$ Group	$C-C(O)H$ Group	CH_3	CH_2 (ii)	CH (ii)	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_2O	Formaldehyde	1	0	1	0	0	0	0	0	0	0	0	0	0	15.64628	15.655	0.00056
C_2H_4O	Acetaldehyde	0	1	1	1	1	0	0	0	0	0	0	0	0	28.18711	28.198	0.00039
C_3H_6O	Propanal	0	1	1	1	1	1	0	1	0	0	0	0	0	40.34481	40.345	0.00000
C_4H_8O	Butanal	0	1	1	1	1	2	0	2	0	0	0	0	0	52.50251	52.491	-0.00022
C_4H_8O	Isobutanal	0	1	1	1	2	0	1	0	2	0	0	0	0	52.60340	52.604	0.00001
$C_5H_{10}O$	Pentanal	0	1	1	1	1	3	0	3	0	0	0	0	0	64.66021	64.682	0.00034
$C_7H_{14}O$	Heptanal	0	1	1	1	1	5	0	5	0	0	0	0	0	88.97561	88.942	-0.00038
$C_8H_{16}O$	Octanal	0	1	1	1	1	6	0	6	0	0	0	0	0	101.13331	101.179	0.00045
$C_8H_{16}O$	2-Ethylhexanal	0	1	1	1	2	4	1	3	3	0	0	0	0	101.20587	101.259	0.00053

Table 15.92. The bond angle parameters of alkyl aldehydes and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HC_aH$ $(C_aH_2(O)$ (i))	2.09132	2.09132	3.5637	-16.39089	18	H	H	0.83008	1	1	1	0.75	1.20470	0				116.87	116.5 (formaldehyde)
$\angle C_bC_aH$ $RC_a(H)=O$	2.86175	2.11323	4.2269	-15.75493 C_a	7	-14.82575 C_b	1	0.86359	0.91771	0.75	1	0.75	1.06267	0				115.52	115.3 (acetaldehyde)
$\angle C_bC_aO$	2.86175	2.27954	4.5826	-16.68412	25	-13.61806	0	0.81549	0.85395 (Eq. (15.114))	1	1	1	0.83472	-1.65376				125.70	124.1 (acetaldehyde)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	109.8 (acetaldehyde)
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_b$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

KETONES ($C_nH_{2n}O,\ n = 1,2,3,4,5...\infty$)

The alkyl ketones, $C_nH_{2n}O$, each have a $C=O$ moiety that comprises a functional group. Each of the two single bonds of carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. The alkyl portion of the alkyl ketone may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in ketones are equivalent to those in branched-chain alkanes.

The $C=O$ and $C-C(O)$ groups are solved by hybridizing the $2s$ and $2p$ AOs of each C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the O AO or between two $C2sp^3$ HOs, respectively, to form a MO permits each participating orbital to decrease in radius and energy. In alkyl ketones, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3) = -14.63489\ eV$ (Eq. (15.25)) and the O AO has an energy of $E(O) = -13.61806\ eV$. To meet the equipotential condition of the union of the $C=O$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the $C=O$-bond MO given by Eq. (15.114) is $c_2(C2sp^3HO\ to\ O) = 0.85395$. The unpaired electrons created by bond breakage of the double $C=O$ bond requires that two times the $O2p$ AO magnetic energy E_{mag} (Eq. (15.60)) be subtracted from the total energy to give $E_D(_{Group})\ (eV)$ for $C=O$.

As in the case with aldehydes, $E_T(atom-atom, msp^3.AO)$ of the $C=O$-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is $-2.69893\ eV$ which is an energy minimum for the double bond between the pair of $C2sp^3$ HO electrons of the C atom and the pair of AO electrons of the O atom. It is given as a linear combination of

the energy contributions corresponding to a double bond, $-1.13379\ eV$ (Eq. (14.247)), and a triple bond, $-1.56513\ eV$ (Eq. (14.342)). The triple bond contribution includes the $C2sp^3$ HO electron of the $C-C(O)$ bond in addition to the pair involved directly in the double bond with O. Consequently, $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-C(O)$-bond MO is $-1.44915\ eV$, corresponding to the energy contributions of the two $C2sp^3$ HOs to the single bond that are equivalent to those of methyl groups, $-0.72457\ eV$ (Eq. (14.151)). Since there are two $C-C(O)$ bonds in ketones versus one in aldehydes, $C_{1o}=C_1$ in Eq. (15.52) for each $C-C(O)$ ketone bond.

The symbols of the functional groups of alkyl ketones are given in Table 15.93. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.55)) parameters of alkyl ketones are given in Tables 15.94, 15.95, and 15.96, respectively. The total energy of each alkyl ketone given in Table 15.97 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.96 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of alkyl ketones determined using Eqs. (15.79-15.108) are given in Table 15.98.

Table 15.93. The symbols of functional groups of alkyl ketones.

Functional Group	Group Symbol
C=O	$C=O$
C-C(O)	$C-C(O)$
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.94. The geometrical bond parameters of alkyl ketones and experimental values [1].

Parameter	$C=O$ Group	$C-C(O)$ Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.312172	2.04740	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.14550	1.43087	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (\AA)$	1.21235	1.51437	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(\AA)$	1.213 (acetone) 1.219 (2-butanone)	1.520 (acetone) 1.518 (2-butanone)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	0.64002	1.46439	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.87298	0.69887	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.95. The MO to HO intercept geometrical bond parameters of alkyl ketones. R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulombic}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$R'C_cH_2(RC_bH_2)C_a=O$	O	-1.34946	0	0	0		1.00000	0.84115	-16.17521		136.09	43.91	65.72	0.53955	0.60595
$R'C_cH_2(RC_bH_2)C_a=O$	C_a	-1.34946	-0.72458	-0.72458	0	-154.41430	0.91771	0.77199	-17.62437	-17.43350	133.02	46.98	61.86	0.61878	0.52672
$H_3C_b-C_a(O)(R')$	C_b	-0.72458	0	0	0	-152.34026	0.91771	0.87495	-15.55033	-15.35946	73.62	106.38	34.98	1.67762	0.246675
$RH_2C_c-H_2C_b-C_a(O)(R')$	C_b	-0.72458	-0.92918	0	0	-153.26945	0.91771	0.82562	-16.47951	-16.28865	67.40	112.60	31.36	1.74821	0.31734
$C-H\ (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\ (CH)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ $(C-C\text{ (a)})$	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ $(C-C\text{ (a)})$	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b(H_2C_c-R')HCH_2-$ $(C-C\text{ (b)})$	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C\text{ (c)})$	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b(H_2C_c-R')HCH_2-$ $(C-C\text{ (d)})$	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C\text{ (e)})$	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b(H_2C_c-R')HCH_2-$ $(C-C\text{ (f)})$	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C\text{ (f)})$	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.96. The energy parameters (eV) of functional groups of alkyl ketones.

Parameters	$C=O$ Group	$C-C(O)$ Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	2	1	3	2	1	1	1	1	1	1	1
n_2	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1
c_2	0.85395	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	2	0	0	1	1	0	0	0	1	1	0
c_4	4	2	1	1	1	2	2	2	2	2	2
c_5	0	0	3	2	1	0	0	0	0	0	0
C_{1o}	0.5	1	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	1	1	1	1	1	1	1	1	1	1	1
$V_e\ (eV)$	-109.17602	-30.19634	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_p\ (eV)$	23.75521	9.50874	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
$T\ (eV)$	41.60126	7.37432	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$V_m\ (eV)$	-20.80063	-3.68716	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(_{AO/HO})\ (eV)$	0	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(_{AO/HO})\ (eV)$	-1.34946	0	0	0	0	0	0	0	0	0	0
$E_T(_{AO/HO})\ (eV)$	1.34946	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(_{H_2MO})\ (eV)$	-63.27071	-31.63534	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom,msp^3.AO)\ (eV)$	-2.69893	-1.44915	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(_{MO})\ (eV)$	-65.96966	-33.08452	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\ (10^{15}\ rad/s)$	57.0928	16.4962	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_K\ (eV)$	37.57947	10.85807	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D\ (eV)$	-0.40003	-0.21568	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}\ (eV)$	0.21462 [27]	0.14655 [28]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}\ (eV)$	-0.29272	-0.14240	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{mag}\ (eV)$	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(_{Group})\ (eV)$	-66.55510	-33.22692	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(_{c_4\ AO/HO})\ (eV)$	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(_{c_5\ AO/HO})\ (eV)$	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(_{Group})\ (eV)$	7.78672	3.95714	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.97. The total bond energies of alkyl ketones calculated using the functional group composition and the energies of Table 15.96 compared to the experimental values [3]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by (15.57).

Formula	Name	$C=O$ Group	$C-C(O)$ Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_3H_6O	Acetone	1	2	2	0	0	0	0	0	0	0	0	0	40.68472	40.672	-0.00031
C_4H_8O	2-Butanone	1	2	2	1	0	1	0	0	0	0	0	0	52.84242	52.84	-0.00005
$C_5H_{10}O$	2-Pentanone	1	2	2	2	0	2	0	0	0	0	0	0	65.00012	64.997	-0.00005
$C_5H_{10}O$	3-Pentanone	1	2	2	2	0	2	0	0	0	0	0	0	65.00012	64.997	-0.00005
$C_5H_{10}O$	3-Methyl-2-butanone	1	2	3	0	1	0	2	0	0	0	0	0	65.10101	65.036	-0.00099
$C_6H_{12}O$	2-Hexanone	1	2	2	2	0	3	0	0	0	0	0	0	77.15782	77.152	-0.00008
$C_6H_{12}O$	3-Hexanone	1	2	2	3	0	3	0	0	0	0	0	0	77.15782	77.138	-0.00025
$C_6H_{12}O$	2-Methyl-3-pentanone	1	2	3	1	1	1	2	0	0	0	0	0	77.25871	77.225	-0.00043
$C_6H_{12}O$	3,3-Dimethyl-2-butanone	1	2	4	0	0	0	0	3	0	0	0	-2	77.29432	77.273	-0.00028
$C_7H_{14}O$	3-Heptanone	1	2	2	4	0	4	0	0	0	0	0	0	89.31552	89.287	-0.00032
$C_7H_{14}O$	4-Heptanone	1	2	0	4	0	4	0	0	0	0	0	0	89.31552	89.299	-0.00018
$C_7H_{14}O$	2,2-Dimethyl-3-pentanone	1	2	4	1	0	1	0	3	0	0	0	-2	89.45202	89.458	0.00007
$C_7H_{14}O$	2,4-Dimethyl-3-pentanone	1	2	4	0	2	0	4	0	0	0	0	0	89.51730	89.434	-0.00093
$C_8H_{16}O$	2,2,4-Trimethyl-3-pentanone	1	2	5	0	1	0	2	3	0	0	0	-2	101.71061	101.660	-0.00049
$C_9H_{18}O$	2-Nonanone	1	2	2	6	0	6	0	0	0	0	0	0	113.63092	113.632	0.00001
$C_9H_{18}O$	5-Nonanone	1	2	2	6	0	6	0	0	0	0	0	0	113.63092	113.675	0.00039
$C_9H_{18}O$	2,6-Dimethyl-4-heptanone	1	2	4	2	2	0	6	0	0	0	0	0	113.77604	113.807	0.00027

Table 15.98. The bond angle parameters of alkyl ketones and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle C_bC_a(O)C_c$	2.86175	2.86175	4.8477	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				115.77	116.0 (acetone)
$\angle C_aC_bC_a(O)$	2.91547	2.86175	4.8374	-16.68412 C_d	25	-16.68412 C_a	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				113.71	113.5 (2-butanone)
$\angle C_aC_aO$	2.86175	2.29100	4.5166	-15.55033	5	-13.61806	O	0.87495	0.85395 (Eq. (15.114))	1	1	1	0.86445	-1.44915				122.07	121.9 (2-butanone)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	108.5 (acetone)
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

CARBOXYLIC ACIDS ($C_nH_{2n}O_2$, $n = 1,2,3,4,5...\infty$)

The alkyl carboxylic acids, $C_nH_{2n}O_2$, comprise a $C=O$ functional group, and the single bond of carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. Formic acid has a $HC=O$ moiety that comprises a more stable $C=O$ functional group and a CH functional group. All carboxylic acids further comprise a $C-OH$ moiety that comprises $C-O$ and OH functional groups. The alkyl portion of the alkyl carboxylic acid may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acids are equivalent to those in branched-chain alkanes.

The CH functional group was solved in the Hydrogen Carbide (CH) section except that the energy of the $C-H$ MO is matched to the carbon-atom contribution to $\Delta E_{H_2MO}(AO/HO)$ and $E_T(atom-atom, msp^3.AO)$ of the $C-O$ group. The alkyl carboxylic acid $C=O$ and $C-C(O)$ groups are equivalent to those given in the Aldehydes section except that $\overline{E}_{Kvib}$ is that of a carboxylic acid. The formic acid $C=O$ group is solved equivalently to that of the alkyl carboxylic acid group, except that $\Delta E_{H_2MO}(AO/HO)$ and $E_T(atom-atom, msp^3.AO)$ correspond to a 25% increase in the donation of charge density from the orbitals of the atoms to the $C=O$ MO due to the presence of a H bound to the carbonyl carbon. Also, $\overline{E}_{Kvib}$ is that corresponding to formic acid. The $C-O$ and OH groups are equivalent to those of alkyl alcohols given in the corresponding section except that the energy of the $C-O$ MO is matched to that of the $C=O$ group and $\overline{E}_{Kvib}$ is that of a carboxylic acid. $\Delta E_{H_2MO}(AO/HO)$ of the $C-O$ group is equal to $E_T(atom-atom, msp^3.AO)$ of the alkyl $C=O$ group in order to match the energies of the corresponding MOs.

As in the case with aldehydes and ketones, $E_T(atom-atom, msp^3.AO)$ of the $C=O$-bond MO in Eq. (15.52) of alky carboxylic acids due to the charge donation from the C and O

atoms to the MO is $-2.69893\ eV$ which is an energy minimum for the double bond between the pair of $C2sp^3$ HO electrons of the C atom and the pair of AO electrons of the carbonyl O atom. It is given as a linear combination of the energy contributions corresponding to a double bond, $-1.13379\ eV$ (Eq. (14.247)), and a triple bond, $-1.56513\ eV$ (Eq. (14.342)). The triple bond contribution includes the energy match of the carbonyl $C2sp^3$ HO electron with the O of the $C-O$-bond MO in addition to the pair involved directly in the double bond with the carbonyl O.

$E_T\left(atom-atom,msp^3.AO\right)$ of the formic acid $C=O$-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is $-3.58557\ eV$. This is also an energy minimum for the double bond between the pair of $C2sp^3$ HO electrons of the C atom and the pair of AO electrons of the carbonyl O atom. It is given as a linear combination of the energy contributions corresponding to a triple bond, $-1.56513\ eV$ (Eq. (14.342)), and a quadruple bond, $-2.02043\ eV$ (Eqs. (15.18-15.21) with $s=4$)) where the bond order components are increased by an integer over that of alkyl carboxylic acids due to the presence of a H bound to the carbonyl carbon.

$E_T\left(atom-atom,msp^3.AO\right)$ of the carboxylic acid $C-C(O)$ group is equivalent to that of alkanes and aldehydes, $-1.85836\ eV$, where both energy contributions are given by Eq. (14.513). It is based on the energy match between the $C2sp^3$ HOs of the carboxylic acid. As in the case of aldehydes, $C_{1o}=2C_1$ in Eq. (15.52).

$E_T\left(atom-atom,msp^3.AO\right)$ of the carboxylic acid $C-O$ group is equivalent to that of alkyl alcohols, $-1.85836\ eV$. It is based on the energy match between the O AO and the $C2sp^3$ HO of a methylene group (the maximum hybridization for a single bond) where both energy contributions are given by Eq. (14.513). $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-O$ group matches that of the $C-C(O)$ group.

The symbols of the functional groups of alkyl carboxylic acids are given in Table 15.99. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl carboxylic acids are given in Tables 15.100, 15.101, and 15.102, respectively. The total energy of each alkyl carboxylic acid given in Table 15.103 was calculated as the sum over the integer multiple of each $E_D(_{Group})$ of Table 15.102 corresponding to functional-group composition of the molecule. For each set of unpaired

electrons created by bond breakage , the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of alkyl carboxylic acids determined using Eqs. (15.79-15.108) are given in Table 15.104.

Table 15.99. The symbols of functional groups of alkyl carboxylic acids.

Functional Group	Group Symbol
CH (formic acid) group	$C-H$ (i)
C-C(O)	$C-C(O)$
C=O (formic acid)	$C=O$ (i)
C=O (alkyl carboxylic acid)	$C=O$ (ii)
(O)C-O	$C-O$
OH group	OH
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH (alkyl) group	$C-H$ (ii)
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.100. The geometrical bond parameters of alkyl carboxylic acids and experimental values [1].

Parameter	$C-H$ (i) Group	$C-C(O)$ Group	$C=O$ (i) Group	$C=O$ (ii) Group	$C-O$ Group	OH Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ (ii) Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.61341	2.04740	1.290799	1.29907	1.73490	1.26430	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.03711	1.43087	1.13613	1.13977	1.31716	0.91808	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (Å)$	1.09763	1.51437	1.20243	1.20628	1.39402	0.971651	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(Å)$	1.097 (formic acid)	1.520 (acetic acid)	1.202 (formic acid)	1.214 (acetic acid)	1.393 (methyl formate)	0.972 (formic acid)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	1.23591	1.46439	0.61267	0.62331	1.12915	0.86925	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.64281	0.69887	0.88018	0.87737	0.75921	0.72615	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.101. The MO to HO intercept geometrical bond parameters of alkyl carboxylic acids. R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$RC_a(O)O-H$	O	-0.92918	0	0	0		1.00000	0.86359	-15.75493		115.09	64.91	64.12	0.55182	0.36625
$HC_a(O)-OH$ ($C=O$ (i))	O	-0.92918	0	0	0		1.00000	0.86359	-15.75493		101.32	78.68	48.58	1.14765	0.16950
$HC_a(O)-OH$ ($C=O$ (i))	C_a	-0.92918	-1.79278	0	0	-154.33765	0.91771	0.77536	-17.54772	-17.35685	93.94	86.06	43.24	1.26386	0.05329
$RH_2C_bC_a(O)-OH$	O	-0.92918	0	0	0		1.00000	0.86359	-15.75493		101.32	78.68	48.58	1.14765	0.16950
$RH_2C_bC_a(O)-OH$	C_a	-0.92918	-1.34946	-0.92918	0	-154.82352	0.91771	0.75447	-18.03358	-17.84271	91.96	88.04	41.90	1.29138	0.02578
$HC_a(OH)=O$ ($C=O$ (i))	O	-1.79278	0	0	0		1.00000	0.81871	-16.61853		137.10	42.90	65.45	0.53635	0.59978
$HC_a(OH)=O$ ($C=O$ (i))	C_a	-1.79278	-0.92918	0	0	-154.33766	0.91771	0.77536	-17.54772	-17.35685	135.24	44.76	63.02	0.58561	0.55053
$RC_bH_2C_a(OH)=O$ ($C=O$ (ii))	O	-1.34946	0	0	0		1.00000	0.84115	-16.17521		137.27	42.73	66.31	0.52193	0.61784
$RC_bH_2C_a(OH)=O$ ($C=O$ (ii))	C_a	-1.34946	-0.92918	-0.92918	0	-154.82352	0.91771	0.75447	-18.03358	-17.84271	133.47	46.53	61.46	0.62072	0.51905
$H-C(O)OH$ (CH (i))	C	-1.79278	-0.92918	0	0	-154.33766	0.91771	0.77536	-17.54772	-17.35685	69.89	110.11	36.09	1.30373	0.26662
$RH_2C_b-C_a(O)OH$	C_a	-0.92918	-1.34946	-0.92918	0	-154.82352	0.91771	0.75447	-18.03358	-17.84271	56.25	123.75	25.37	1.85002	0.41915
$H_3C_b-C_a(O)OH$	C_b	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	72.27	107.73	34.17	1.69388	0.26301
$RH_2C_cH_2C_b-C_a(O)OH$	C_b	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	65.99	114.01	30.58	1.76270	0.33183
$C-H\ (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\ (CH)$ (ii)	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ ($C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ ($C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.102. The energy parameters (eV) of functional groups of alkyl carboxylic acids.

Parameters	$C-H$ (i) Group	$C-C(O)$ Group	$C=O$ (i) Group	$C=O$ (ii) Group	$C-O$ Group	OH Group	CH_3 Group	CH_2 Group	$C-H$ (ii) Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	1	2	2	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.75	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	0.75	1	1	1	1	1	1	1	1	1
c_2	0.91771	0.91771	0.85395	0.85395	0.85395	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	2	2	0	1	0	1	1	0	0	0	1	1	0
c_4	1	2	4	4	2	1	1	1	1	2	2	2	2	2	2
c_5	1	0	0	0	0	1	3	2	1	0	0	0	0	0	0
C_{1o}	0.75	1	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$V_e\ (eV)$	-36.74167	-30.19634	-112.61934	-111.25473	-35.08488	-40.92709	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_p\ (eV)$	13.11890	9.50874	23.95107	23.87467	10.32968	14.81988	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
$T\ (eV)$	11.38634	7.37432	43.62389	42.82081	10.11150	16.18567	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$V_m\ (eV)$	-5.69317	-3.68716	-21.81195	-21.41040	-5.05575	-8.09284	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(_{AO/HO})\ (eV)$	-14.63489	-14.63489	0	0	-14.63489	-13.6181	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(_{AO/HO})\ (eV)$	-0.92918	0	-3.58557	-2.69893	-2.69893	0	0	0	0	0	0	0	0	0	0
$E_T(_{AO/HO})\ (eV)$	-13.70571	-14.63489	3.58557	2.69893	-11.93596	-13.6181	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(_{H_2MO})\ (eV)$	-31.63530	-31.63534	-63.27075	-63.27074	-31.63541	-31.63247	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom,msp^3.AO)\ (eV)$	0	-1.85836	-3.58557	-2.69893	-1.85836	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(_{MO})\ (eV)$	-31.63537	-33.49373	-66.85630	-65.96966	-33.49373	-31.63537	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\ (10^{15}\ rad/s)$	26.0575	23.3291	60.9581	59.4034	24.3637	44.1776	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_K\ (eV)$	17.15150	15.35563	40.12366	39.10034	16.03660	29.07844	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D\ (eV)$	-0.25920	-0.25966	-0.41891	-0.40804	-0.26535	-0.33749	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}\ (eV)$	0.35532 (Eq. (13.458))	0.10502 [29]	0.21945 [30]	0.21077 [12]	0.14010 [31]	0.46311 [17-18]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}\ (eV)$	-0.08153	-0.20715	-0.30918	-0.30266	-0.19530	-0.10594	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{mag}\ (eV)$	0.14803	0.14803	0.11441	0.11441	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(_{Group})\ (eV)$	-31.71690	-33.70088	-67.47466	-66.57498	-33.68903	-31.74130	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(_{c_4\ AO/HO})\ (eV)$	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-13.6181	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(_{c_5\ AO/HO})\ (eV)$	-13.59844	0	0	0	0	-13.59844	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(_{Group})\ (eV)$	3.48357	4.43110	8.70628	7.80660	4.41925	4.41035	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.103. The total bond energies of alkyl carboxylic acids calculated using the functional group composition and the energies of Table 15.102 compared to the experimental values [3]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(_{Group})\ (eV)$ values based on composition is given by (15.57).

Formula	Name	$C-H$ (i) Group	$C-C(O)$ Group	$C=O$ (i) Group	$C=O$ (ii) Group	$C-O$ Group	OH Group	CH_3	CH_2	CH (ii)	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_2O_2	Formic acid	1	0	1	0	1	1	0	0	0	0	0	0	0	0	0	0	21.01945	21.036	0.00079
$C_2H_4O_2$	Acetic acid	0	1	0	1	1	1	1	0	0	0	0	0	0	0	0	0	33.55916	33.537	-0.00066
$C_3H_6O_2$	Propanoic acid	0	1	0	1	1	1	1	1	0	1	0	0	0	0	0	0	45.71686	45.727	0.00022
$C_4H_8O_2$	Butanoic acid	0	1	0	1	1	1	1	2	0	2	0	0	0	0	0	0	57.87456	57.883	0.00015
$C_5H_{10}O_2$	Pentanoic acid	0	1	0	1	1	1	1	3	0	3	0	0	0	0	0	0	70.03226	69.995	-0.00053
$C_5H_{10}O_2$	3-Methylbutanoic acid	0	1	0	1	1	1	2	1	1	0	3	0	0	0	0	0	70.10482	70.183	0.00111
$C_5H_{10}O_2$	2,2-Dimethylpropanoic acid	0	1	0	1	1	1	3	0	0	0	0	3	0	0	0	-1	70.31679	69.989	-0.00468
$C_6H_{12}O_2$	Hexanoic acid	0	1	0	1	1	1		4	0	4	0	0	0	0	0	0	82.18996	82.149	-0.00050
$C_7H_{14}O_2$	Heptanoic acid	0	1	0	1	1	1	1	5	0	5	0	0	0	0	0	0	94.34766	94.347	0.00000
$C_8H_{16}O_2$	Octanoic acid	0	1	0	1	1	1	1	6	0	6	0	0	0	0	0	0	106.50536	106.481	-0.00022
$C_9H_{18}O_2$	Nonanoic acid	0	1	0	1	1	1	1	7	0	7	0	0	0	0	0	0	118.66306	118.666	0.00003
$C_{10}H_{20}O_2$	Decanoic acid	0	1	0	1	1	1	1	8	0	8	0	0	0	0	0	0	130.82076	130.795	-0.00020
$C_{12}H_{24}O_2$	Dodecanoic acid	0	1	0	1	1	1	1	10	0	10	0	0	0	0	0	0	155.13616	155.176	0.00026
$C_{14}H_{28}O_2$	Tetradecanoic acid	0	1	0	1	1	1	1	12	0	12	0	0	0	0	0	0	179.45156	179.605	0.00085
$C_{15}H_{30}O_2$	Pentadecanoic acid	0	1	0	1	1	1	1	13	0	13	0	0	0	0	0	0	191.60926	191.606	-0.00002
$C_{16}H_{32}O_2$	Hexadecanoic acid	0	1	0	1	1	1	1	14	0	14	0	0	0	0	0	0	203.76696	203.948	0.00089
$C_{18}H_{36}O_2$	Stearic acid	0	1	0	1	1	1	1	16	0	16	0	0	0	0	0	0	228.08236	228.298	0.00094
$C_{20}H_{40}O_2$	Eicosanoic acid	0	1	0	1	1	1	1	18	0	18	0	0	0	0	0	0	252.39776	252.514	0.00046

Table 15.104. The bond angle parameters of alkyl carboxylic acids and experimental values [1] In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp θ (°)
$\angle HC'_aO_a$ $((CH\ (i);\ C=O\ (i))$	2.06598	2.27227	3.8816	-15.55033 C'_a	5	-13.61806	O	0.87495	0.85395 (Eq. (15.114))	0.75	1	0.75	0.97600	0				126.88	124.1 (formic acid)
$\angle HC'_aO_b$ $((CH\ (i))$	2.06598	2.63431	3.8816	-15.55033 C'_a	5	-13.61806	O	0.87495	0.85395 (Eq. (15.114))	0.75	1	0.75	0.97600	0				110.76	
$\angle O_aC'_aO_b$	2.27227	2.63431	4.3243	-16.61853 O_a	23	-15.75493 O_b	7	0.81871	0.86359	1	1	1	0.84115	-1.44915				123.44	124.9 (formic acid)
$\angle C'_aO_bH$ $((CH\ (i);\ C=O\ (i))$	2.63431	1.83616	3.6405	-14.82575	1	-14.82575	1	1	0.91771	0.75	1	0.75	0.91771	0				107.71	106.3 (formic acid)
$\angle C'_bC'_aO_a$	2.86175	2.27954	4.5826	-16.68411	24	-13.61806	O	0.81549	0.85395 (Eq. (15.114))	1	1	1	0.83472	-1.65376				125.70	126.6 (acetic acid)
$\angle C'_bC'_aO_b$	2.86175	2.63431	4.4944	-15.75493	7	-13.61806	O	0.86359	0.85395 (Eq. (15.114))	1	1	1	0.85877	-1.44915				109.65	110.6 (acetic acid)
$\angle O_aC'_aO_b$	2.27954	2.63431	4.3818	-16.17521 O_a	12	-15.75493 O_b	7	0.84115	0.86359	1	1	1	0.85257	-1.44915				126.03	
Methylene $\angle HC'_aH$	2.11106	2.11106	3.4252	-15.75493		H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C'_aC'_bC'_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C'_aC'_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC'_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	108.5 (acetone)
$\angle C'_aC'_bC'_c$															70.56			109.44	
$\angle C'_aC'_bH$															70.56			109.44	
$\angle C'_bC'_aC'_c$ iso C'_a	2.91547	2.91547	4.7958	-16.68412 C'_b	25	-16.68412 C'_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C'_bC'_aH$ iso C'_a	2.91547	2.11323	4.1633	-15.55033 C'_a	5	-14.82575 C'_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C'_aC'_bH$ iso C'_a	2.91547	2.09711	4.1633	-15.55033 C'_b	5	-14.82575 C'_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C'_bC_aC_c$ tert C'_a	2.90327	2.90327	4.7958	-15.55033 C'_b	5	-14.82575 C'_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C'_bC'_aC'_d$															72.50			107.50	

CARBOXYLIC ACID ESTERS ($C_nH_{2n}O_2$, $n = 1,2,3,4,5...\infty$)

The alkyl carboxylic acid esters, $C_nH_{2n}O_2$, comprise a $C=O$ functional group, and the single bond of carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. Formic acid ester has a $HC=O$ moiety that comprises a more stable $C=O$ functional group and a CH functional group. All carboxylic acid esters further comprise a COR moiety that comprises a $C-O$ functional group and three types of $O-R$ functional groups, one for R comprising methyl, one for R comprising an alkyl ester group of a formate, and one for R comprising an alkyl ester group of an alkyl carboxylate. The alkyl portion of the alkyl carboxylic acid ester may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acid esters are equivalent to those in branched-chain alkanes.

The CH functional group is equivalent to that of formic acid. The alkyl carboxylic acid ester $C=O$ and $C-C(O)$ groups are equivalent to those given in the Carboxylic Acids section. The formic acid ester $C=O$ group is equivalent to that given in the Carboxylic Acids section except that $\overline{E}_{Kvib}$ is that corresponding to a formic acid ester. The $C-O$ group is equivalent to that given in the Carboxylic Acids section except that the parameters corresponding to oscillation of the bond in the transition state, $\overline{E}_D$ (eV) and $\overline{E}_{Kvib}$, are those of a carboxylic acid ester. As in the case with the alkyl ethers, each $O-C$ group is solved by hybridizing the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the O AO to form a MO permits each participating orbital to decrease in radius and energy. To meet the equipotential condition of the union of the $O-C$ H_2-type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor c_2 of Eq. (15.51) for the $O-C$-bond MO given by Eq. (15.114) is $c_2(C2sp^3HO\ to\ O) = 0.85395$.

$E_T(atom-atom,msp^3.AO)$ (Eq. (15.52)) of (1) the $C=O$ group of alky carboxylic acid esters, (2) the $C=O$ group of formic acid esters, (3) the alkyl carboxylic acid ester $C-C(O)$ group, and (4) the carboxylic acid ester $C-O$ group are equivalent to those of the corresponding carboxylic acids. The values given in the Carboxylic Acids section are $-2.69893\ eV$, $-3.58557\ eV$, $-1.85836\ eV$, and $-1.85836\ eV$, respectively. $E_T(atom-atom,msp^3.AO)$ of the $C-O$ group matches that of the $C-C(O)$ group. Also, as in the case of aldehydes, $C_{1o}=2C_1$ in Eq. (15.52) for the $C-C(O)$ group.

$E_T(atom-atom,msp^3.AO)$ of the $O-C$-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is $-1.13379\ eV$ for the $O-CH_3$ group of formate and alkyl carboxylates, $-1.44915\ eV$ for the $O-R$ group of alkyl carboxylates, and $-1.85836\ eV$ for the $O-R$ group of alkyl formates, where R is an alkyl group. Each is based on the energy match between the O AO, initially at the Coulomb potential of a proton and an electron (Eqs. (1.236) and (10.162), respectively), the $C2sp^3$ HO of the methyl or alkyl ester group, and the carbonyl carbon. The increasing energy contributions to the single bond correspond to the increasing hybridization of linear combinations of increasing bond order. The energy contributions corresponding to one half of a double bond and those of the methyl-methyl and methylene-methylene bonds are $-1.13379\ eV$ (Eq. (14.247)), two times $-0.72457\ eV$ (Eq. (14.151)), and two times $-0.92918\ eV$ (Eq. (14.513)), respectively.

The symbols of the functional groups of alkyl carboxylic acid esters are given in Table 15.105. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl carboxylic acid esters are given in Tables 15.106, 15.107, and 15.108, respectively. The total energy of each alkyl carboxylic acid ester given in Table 15.109 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.108 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage , the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of alkyl carboxylic acid esters determined using Eqs. (15.79-15.108) are given in Table 15.110.

Table 15.105. The symbols of functional groups of alkyl carboxylic acid esters.

Functional Group	Group Symbol
CH (formic acid ester) group	$C-H$ (i)
C-C(O)	$C-C(O)$
C=O (formic acid ester)	$C=O$ (i)
C=O (alkyl carboxylic acid ester)	$C=O$ (ii)
(O)C-O	$C-O$
O-CH_3	$O-C$ (i)
O-R (formic acid ester)	$O-C$ (ii)
O-R (alkyl acid ester)	$O-C$ (iii)
OH group	OH
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH (alkyl) group	$C-H$ (ii)
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.106. The geometrical bond parameters of alkyl carboxylic acid esters and experimental values [1].

Parameter	$C-H$ (i) Group	$C-C(O)$ Group	$C=O$ (i) Group	$C=O$ (ii) Group	$C-O$ Group	$O-C$ (i) Group	$O-C$ (ii) Group	$O-C$ (iii) Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ (ii) Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.61341	2.04740	1.290799	1.29907	1.73490	1.82683	1.78255	1.80717	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.03711	1.43087	1.13613	1.13977	1.31716	1.35160	1.33512	1.34431	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ (Å)	1.09763	1.51437	1.20243	1.20628	1.39402	1.43047	1.41303	1.42276	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.101 (methyl formate)	1.520 (acetic acid)	1.206 (methyl formate)	1.214 (acetic acid)	1.393 (avg. methyl formate)	1.393 (avg. methyl formate)	1.393 (avg. methyl formate)	1.393 (avg. methyl formate)	1.08 (methyl formate) 1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	1.23591	1.46439	0.61267	0.62331	1.12915	1.22901	1.18107	1.20776	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.64281	0.69887	0.88018	0.87737	0.75921	0.73986	0.74900	0.74388	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.107. The MO to HO intercept geometrical bond parameters of alkyl carboxylic acid esters. R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom, msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$RC_a(O)O-C_bH_3$ $(O-C$ (i))	O	-0.92918	-0.56690	0	0		1.00000	0.83360	-16.32183		90.63	89.37	42.70	1.34246	0.00914
$RC_a(O)O-C_bH_3$ $(O-C$ (i))	C'_b	-0.56690	0	0	0	-152.18259	0.91771	0.88392	-15.39265	-15.20178	95.01	84.99	45.76	1.27445	0.07716
$HC_a(O)O-C_bH_2C_cH_2R$ $(O-C$ (ii))	O	-0.92918	-0.92918	0	0		1.00000	0.81549	-16.68412		93.09	86.91	43.59	1.29113	0.04399
$HC_a(O)O-C_bH_2C_cH_2R$ $(O-C$ (ii))	C'_b	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	93.09	86.91	43.59	1.29113	0.04399
$R'C_a(O)O-C_bH_2C_cH_2R$ $(O-C$ (iii))	O	-0.92918	-0.72457	0	0		1.00000	0.82562	-16.47951		91.72	88.28	43.10	1.31951	0.02480
$R'C_a(O)O-C_bH_2C_cH_2R$ $(O-C$ (iii))	C'_b	-0.72457	-0.92918	0	0	-153.26945	0.91771	0.82562	-16.47951	-16.28864	91.72	88.28	43.10	1.31951	0.02480
$HC_a(O)-OC_bH_3$ $(C=O$ (i)) $(O-C$ (i))	O	-0.92918	-0.56690	0	0		1.00000	0.83360	-16.32183		98.97	81.03	46.82	1.18716	0.13000
$HC_a(O)-OC_bH_3$ $(C=O$ (i)) $(O-C$ (i))	C'_a	-0.92918	-1.79278	0	0	-154.33765	0.91771	0.77536	-17.54772	-17.35685	93.94	86.06	43.24	1.26386	0.05329
$HC_a(O)-OR$ $(C=O$ (i)) $(O-C$ (ii))	O	-0.92918	-0.92918	0	0		1.00000	0.81549	-16.68412		97.48	82.52	45.73	1.21100	0.10616
$HC_a(O)-OR$ $(C=O$ (i)) $(O-C$ (ii))	C'_a	-1.79278	-0.92918	0	0	-154.33765	0.91771	0.77536	-17.54772	-17.35685	93.94	86.06	43.24	1.26386	0.05329
$R'H_2C_bC_a(O)-OC_bH_3$ $(C=O$ (ii)) $(O-C$ (i))	O	-0.92918	-0.56690	0	0		1.00000	0.83360	-16.32183		98.97	81.03	46.82	1.18716	0.13000
$R'H_2C_bC_a(O)-OC_bH_3$ $(C=O$ (ii)) $(O-C$ (i))	C'_a	-0.92918	-1.34946	-0.92918	0	-154.82352	0.91771	0.75447	-18.03358	-17.84271	91.96	88.04	41.90	1.29138	0.02578
$R'H_2C_bC_a(O)-OC_bH_2C_cH_2R$ $(C=O$ (ii)) $(O-C$ (iii))	O	-0.92918	-0.72457	0	0		1.00000	0.82562	-16.47951		98.32	81.68	46.34	1.19766	0.11949
$R'H_2C_bC_a(O)-OC_bH_2C_cH_2R$ $(C=O$ (ii)) $(O-C$ (iii))	C'_a	-0.92918	-1.34946	-0.92918	0	-154.82352	0.91771	0.75447	-18.03358	-17.84271	91.96	88.04	41.90	1.29138	0.02578
$HC_a(OR)=O$ $(C=O$ (i))	O	-1.79278	0	0	0		1.00000	0.81871	-16.61853		137.10	42.90	65.45	0.53635	0.59978
$HC_a(OR)=O$ $(C=O$ (i))	C'_a	-1.79278	-0.92918	0	0	-154.33766	0.91771	0.77536	-17.54772	-17.35685	135.24	44.76	63.02	0.58561	0.55053
$R'C_bH_2C_a(OR)=O$ $(C=O$ (ii))	O	-1.34946	0	0	0		1.00000	0.84115	-16.17521		137.27	42.73	66.31	0.52193	0.61784
$R'C_bH_2C_a(OR)=O$ $(C=O$ (ii))	C'_a	-1.34946	-0.92918	-0.92918	0	-154.82352	0.91771	0.75447	-18.03358	-17.84272	133.47	46.53	61.46	0.62072	0.51905
$H-C(O)OR$ $(C'H$ (i))	C'	-1.79278	-0.92918	0	0	-154.33766	0.91771	0.77536	-17.54772	-17.35685	69.89	110.11	36.09	1.30373	0.26662
$R'H_2C_b-C_a(O)OR$	C'_a	-0.92918	-1.34946	-0.92918	0	-154.82352	0.91771	0.75447	-18.03358	-17.84272	56.25	123.75	25.37	1.85002	0.41915
$H_3C_b-C_a(O)OR$	C'_b	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	72.27	107.73	34.17	1.69388	0.26301
$R'H_2C_cH_2C_b-C_a(O)OR$	C'_b	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	65.99	114.01	30.58	1.76270	0.33183
$C'-H$ $(C'H_3)$	C'	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C'-H$ $(C'H_2)$	C'	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C-H$ (CH) (ii)	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.108. The energy parameters (eV) of functional groups of alkyl carboxylic acid esters.

Parameters	$C-H$ (i) Group	$C-C(O)$ Group	$C=O$ (i) Group	$C=O$ (ii) Group	$C-O$ Group	$O-C$ (i) Group	$O-C$ (ii) Group	$O-C$ (iii) Group	CH_3 Group	CH_2 Group	$C-H$ (ii) Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	1	2	2	1	1	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	0	0	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.75	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
c_2	0.91771	0.91771	0.85395	0.85395	0.85395	0.85395	0.85395	0.85395	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	2	2	0	0	0	0	0	1	1	0	0	0	1	1	0
c_4	1	2	4	4	2	2	2	2	1	1	1	2	2	2	2	2	2
c_5	1	0	0	0	0	0	0	0	3	2	1	0	0	0	0	0	0
C_{1o}	0.75	1	0.5	0.5	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
V_e (eV)	-36.74167	-30.19634	-112.61934	-111.25473	-35.08488	-32.67173	-33.78830	-33.15757	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	13.11890	9.50874	23.95107	23.87467	10.32968	10.06642	10.19070	10.12103	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	11.38634	7.37432	43.62389	42.82081	10.11150	8.94219	9.47754	9.17389	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_m (eV)	-5.69317	-3.68716	-21.81195	-21.41040	-5.05575	-4.47110	-4.73877	-4.58695	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(AO/HO)$ (eV)	-14.63489	-14.63489	0	0	-14.63489	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(AO/HO)$ (eV)	-0.92918	0	-3.58557	-2.69893	-2.69893	-1.13379	-1.85836	-1.44915	0	0	0	0	0	0	0	0	0
$E_T(AO/HO)$ (eV)	-13.70571	-14.63489	3.58557	2.69893	-11.93596	-13.50110	-12.77653	-13.18574	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(H_2MO)$ (eV)	-31.63530	-31.63534	-63.27075	-63.27074	-31.63541	-31.63531	-31.63536	-31.63533	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom,msp^3.AO)$ (eV)	0	-1.85836	-3.58557	-2.69893	-1.85836	-1.13379	-1.85836	-1.44915	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(MO)$ (eV)	-31.63537	-33.49373	-66.85630	-65.96966	-33.49373	-32.76916	-33.49373	-33.08452	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω $(10^{15}\ rad/s)$	26.0575	23.3291	60.9581	59.4034	12.7926	21.4553	22.7749	12.0329	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	17.15150	15.35563	40.12366	39.10034	8.42030	14.12224	14.99085	7.92028	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D$ (eV)	-0.25920	-0.25966	-0.41891	-0.40804	-0.19228	-0.24362	-0.25655	-0.18420	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}$ (eV)	0.35532 (Eq. (13.458))	0.10502 [29]	0.21747 [32]	0.21077 [12]	0.14965 [32]	0.11469 [32]	0.11469 [32]	0.16118 [4]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}$ (eV)	-0.08153	-0.20715	-0.31017	-0.30266	-0.11745	-0.18628	-0.19921	-0.10361	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mag} (eV)	0.14803	0.14803	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(Group)$ (eV)	-31.71690	-33.70088	-67.47664	-66.57498	-33.61118	-32.95544	-33.69294	-33.18813	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(c_4\ AO/HO)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(c_5\ AO/HO)$ (eV)	-13.59844	0	0	0	0	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(Group)$ (eV)	3.48357	4.43110	8.70826	7.80660	4.34141	3.68566	4.42316	3.91835	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.109. *The total bond energies of alkyl carboxylic acid esters calculated using the functional group composition and the energies of* Table 15.108 compared to the experimental values [3]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(_{Group})$ (eV) values based on composition is given by (15.57).

Formula	Name	$C-H$ (i) Group	$C-C(O)$ Group	$C=O$ (i) Group	$C=O$ (ii) Group	$C-O$ Group	$O-C$ (i) Group	$O-C$ (ii) Group	$O-C$ (iii) Group	CH_3	CH_2	CH (ii)	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_2H_4O_2$	Methyl formate	1	1	1	0	1	1	0	0	1	0	0	0	0	0	0	0	0	0	32.71076	32.762	0.00156
$C_3H_6O_2$	Methyl acetate	0	1	1	1	1	0	0	0	2	0	0	0	0	0	0	0	0	0	45.24849	45.288	0.00087
$C_6H_{12}O_2$	Methyl pentanoate	0	1	1	1	1	0	0	0	2	3	0	3	0	0	0	0	0	0	81.72159	81.726	0.00005
$C_7H_{14}O_2$	Methyl hexanoate	0	1	1	1	1	0	0	0	2	4	0	4	0	0	0	0	0	0	93.87929	93.891	0.00012
$C_8H_{16}O_2$	Methyl heptanoate	0	1	1	1	1	0	0	0	2	5	0	5	0	0	0	0	0	0	106.03699	106.079	0.00040
$C_9H_{18}O_2$	Methyl octanoate	0	1	1	1	1	0	0	0	2	6	0	6	0	0	0	0	0	0	118.19469	118.217	0.00018
$C_{10}H_{20}O_2$	Methyl nonanoate	0	1	1	1	1	0	0	0	2	7	0	7	0	0	0	0	0	0	130.35239	130.373	0.00016
$C_{11}H_{22}O_2$	Methyl decanoate	0	1	1	1	1	0	0	0	2	8	0	8	0	0	0	0	0	0	142.51009	142.523	0.00009
$C_{12}H_{24}O_2$	Methyl undecanoate	0	1	1	1	1	0	0	0	2	9	0	9	0	0	0	0	0	0	154.66779	154.677	0.00006
$C_{13}H_{26}O_2$	Methyl dodecanoate	0	1	1	1	1	0	0	0	2	10	0	10	0	0	0	0	0	0	166.82549	166.842	0.00010
$C_{14}H_{28}O_2$	Methyl tridecanoate	0	1	1	1	1	0	0	0	2	11	0	11	0	0	0	0	0	0	178.98319	179.000	0.00009
$C_{15}H_{30}O_2$	Methyl tetradecanoate	0	1	1	1	1	0	0	0	2	12	0	12	0	0	0	0	0	0	191.14089	191.170	0.00015
$C_{16}H_{32}O_2$	Methyl pentadecanoate	0	1	1	1	1	0	0	0	2	13	0	13	0	0	0	0	0	0	203.29859	203.356	0.00028
$C_4H_8O_2$	Propyl formate	0	1	1	1	1	0	0	0	1	2	1	2	0	0	0	0	0	0	57.76366	57.746	-0.00030
$C_4H_8O_2$	Ethyl acetate	0	1	0	1	1	0	0	1	2	1	0	1	0	0	0	0	0	0	57.63888	57.548	-0.00157
$C_5H_{10}O_2$	Isopropyl acetate	0	1	0	0	1	0	0	1	3	0	1	0	2	0	0	0	0	0	69.89747	69.889	-0.00013
$C_5H_{10}O_2$	Ethyl propanoate	0	1	0	1	1	0	0	1	2	2	0	2	0	0	0	0	0	0	69.79658	69.700	-0.00139
$C_6H_{12}O_2$	Butyl acetate	0	1	0	1	1	0	0	1	2	3	0	3	0	0	0	0	0	0	81.95428	81.873	-0.00099
$C_6H_{12}O_2$	t-Butyl acetate	0	1	0	1	1	0	0	1	4	0	0	0	0	3	0	0	0	0	82.23881	82.197	-0.00051
$C_6H_{12}O_2$	Methyl 2,2-dimethylpropanoate	0	1	0	1	1	1	0	0	4	0	0	0	0	3	0	0	0	-1	82.00612	81.935	-0.00087
$C_7H_{14}O_2$	Ethyl pentanoate	0	1	0	1	1	0	0	1	2	6	0	6	0	0	0	0	0	0	94.11198	94.033	-0.00084
$C_7H_{14}O_2$	Ethyl 3-methylbutanoate	0	1	0	1	1	0	0	1	3	2	1	1	3	0	0	0	0	0	94.18454	94.252	0.00072
$C_7H_{14}O_2$	Ethyl 2,2-dimethylpropanoate	0	1	0	1	1	0	0	1	4	1	0	1	0	3	0	0	0	-1	94.39651	94.345	-0.00054
$C_8H_{16}O_2$	Isobutyl isobutanoate	0	1	0	1	1	0	0	1	4	1	2	0	5	0	0	0	0	0	106.44313	106.363	-0.00075
$C_8H_{16}O_2$	Propyl pentanoate	0	1	0	1	1	0	0	1	2	5	0	5	0	0	0	0	0	0	106.26968	106.267	-0.00003
$C_8H_{16}O_2$	Isopropyl pentanoate	0	1	0	1	1	0	0	1	3	3	1	3	2	0	0	0	0	0	106.37057	106.384	0.00013
$C_9H_{18}O_2$	Butyl pentanoate	0	1	0	1	1	0	0	1	2	6	0	6	0	0	0	0	0	0	118.42738	118.489	0.00052
$C_9H_{18}O_2$	sec-Butyl pentanoate	0	1	0	1	1	0	0	1	3	4	1	4	2	0	0	0	0	0	118.52827	118.624	0.00081
$C_9H_{18}O_2$	Isobutyl pentanoate	0	1	0	1	1	0	0	1	3	4	1	3	3	0	0	0	0	0	118.49994	118.576	0.00064

Table 15.110. The bond angle parameters of alkyl carboxylic acid esters and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HC_bO_b$ (CH (i); $C=O$ (i))	2.09711	2.70321	3.9463	-15.75493 C_b	7	-13.61806	O	0.86359	0.85395 (Eq. (15.114))	0.75	1	0.75	0.98884	0				109.95	110 (methyl formate)
$\angle O_aC_aO_b$ (CH (i); $C=O$ (i))	2.27227	2.63431	4.4045	-16.61853 O_a	23	-16.68412 O_b	25	0.81871	0.81549	1	1	1	0.81710	-1.65376				127.56	127 (methyl formate)
$\angle C_bO_bC_a$ (CH (i); $C=O$ (i))	2.70321	2.63431	4.4833	-16.32183 C_b	16	-18.47690 C_a	50	0.83360	0.73637	1	1	1	0.78498	-1.85836				114.27	114 (methyl formate)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	108.5 (acetone)
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

AMIDES ($C_nH_{2n+1}NO,\ n=1,2,3,4,5...\infty$)

The alkyl amides, $C_nH_{2n+1}NO$, comprise a $C=O$ functional group, and the single bond of carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. Formamide has a $HC=O$ moiety that comprises a more stable $C=O$ functional group and a CH functional group that is equivalent to that of the CH (i) of aldehydes given in the corresponding section. It is also equivalent to that of the iso-CH group of branched-chain-alkyl portion of the alkyl amide except that E_{mag} (Eq. (15.58)) is not subtracted from $E_D(Group)$. All amides further comprise a $C-NH_2$ moiety that comprises a NH_2 functional group and two types of $C-N$ functional groups, one for formamide and the other for alkyl amides ($RC(O)NH_2$ where R is alkyl). The alkyl portion of the alkyl amide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in amides are equivalent to those in branched-chain alkanes.

The NH_2 functional group was solved in the Dihydrogen Nitride (NH_2) section except that the energy of the $N-H$ MO is matched to the nitrogen-atom contribution to $\Delta E_{H_2MO}(AO/HO)$ and $E_T(atom-atom,msp^3.AO)$ of the $C-N$ group. Both alkyl amide $C=O$ groups and the $C-C(O)$ group are equivalent to those given in the Carboxylic Acid Esters section except that $\overline{E}_{Kvib}$ of the $C-C(O)$ group is matched to that of an amide. The $C-N$ groups are equivalent to those of alkyl amines given in the corresponding section except that the energy of the $C-N$ MO is matched to that of the $C=O$ group and $\overline{E}_{Kvib}$ is that of a amide. $\Delta E_{H_2MO}(AO/HO)$ of the $C-N$ group is equal to $E_T(atom-atom,msp^3.AO)$ of the alkyl $C=O$ and $C-N$ groups in order to match the energies of the corresponding MOs.

As in the case of primary amines, each $C-N$ group is solved by hybridizing the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of

electrons between the $C2sp^3$ HO and the N AO to form a MO permits each participating orbital to decrease in radius and energy. To meet the equipotential condition of the union of the $C-N$ H_2-type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor c_2 of Eq. (15.52) for the $C-N$-bond MO given by Eq. (15.114) is $c_2(C2sp^3HO\ to\ N) = 0.91140$.

$E_T(atom-atom, msp^3.AO)$ (Eq. (15.52)) of the $C=O$ group of alky amides and the $C=O$ group of formamide are equivalent to those of the corresponding carboxylic acids and esters. The values given in the Carboxylic Acids section are $-2.69893\ eV$ and $-3.58557\ eV$, respectively.

$E_T(atom-atom, msp^3.AO)$ of the amide $C-C(O)$ group is the same as alkanes, aldehydes, carboxylic acids, and carboxylic acid esters, $-1.85836\ eV$, where both energy contributions are given by Eq. (14.513). Also, as in the case of aldehydes, $C_{1_o} = 2C_1$ in Eq. (15.52).

In order to match energy throughout the chain of the amide molecule, $E_T(atom-atom, msp^3.AO)$ of the $C-N$-bond MO in Eq. (15.52) due to the charge donation from the C and N atoms to the MO is $-1.65376\ eV$. It is based on the energy match between the $C2sp^3$ HO of the carbonyl and the primary amino group NH_2. It is given by the linear combination of $-0.92918\ eV$ (Eq. (14.513)) which matches the contiguous $C-C(O)$ or $HC(O)$ group and $-0.72457\ eV$ (Eq. (14.151)), the contribution of a primary amino group given in the Primary Amines section.

The symbols of the functional groups of alkyl amides are given in Table 15.111. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl amides are given in Tables 15.112, 15.113, and 15.114, respectively. The total energy of each alkyl amide given in Table 15.115 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.114 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl amides determined using Eqs. (15.79-15.108) are given in Table 15.116.

Table 15.111. The symbols of functional groups of alkyl amides.

Functional Group	Group Symbol
CH (formamide) group	$C-H$ (i)
C-C(O)	$C-C(O)$
C=O (formamide)	$C=O$ (i)
C=O (alkyl amide)	$C=O$ (ii)
(O)C-N (formamide)	$C-N$ (i)
(O)C-N (alkyl amide)	$C-N$ (ii)
NH_2 group	NH_2
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH (alkyl) group	$C-H$ (ii)
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.112. The geometrical bond parameters of alkyl amides and experimental values [1].

Parameter	$C-H$ (i) Group	$C-C(O)$ Group	$C=O$ (i) Group	$C=O$ (ii) Group	$C-N$ (i) Group	$C-N$ (ii) Group	NH_2 Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ (ii) Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.67465	2.04740	1.290799	1.29907	1.70920	1.75370	1.32297	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.05661	1.43087	1.13613	1.13977	1.30736	1.32427	0.97065	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (\AA)$	1.11827	1.51437	1.20243	1.20628	1.38365	1.40155	1.02729	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(\AA)$	1.125 (formamide)	1.519 (acetamide) 1.520 (N-methylacetamide)	1.212 (formamide)	1.220 (acetamide) 1.225 (N-methylacetamide)	1.368 (formamide)	1.380 (acetamide)	1.027 (formamide) 1.022 (acetamide)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	1.29924	1.46439	0.61267	0.62331	1.10098	1.14968	0.89894	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.63095	0.69887	0.88018	0.87737	0.76490	0.75513	0.73369	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.113. The MO to HO intercept geometrical bond parameters of alkyl amides. R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$RC(O)N(H)-H$ ($C=O$ (i) and (ii))	N	-0.82688	0	0	0		0.93084	0.86923	-15.65263		113.90	66.10	62.13	0.61843	0.35222
$HC(O)-NH_2$ ($C=O$ (i)) ($C-N$ (i))	N	-0.82688	0	0	0		0.93084	0.86923	-15.65263		103.93	76.07	50.02	1.09814	0.20922
$HC(O)-NH_2$ ($C=O$ (i)) ($C-N$ (i))	C	-0.82688	-1.79278	0	0	-154.23535	0.91771	0.77991	-17.44541	-17.25455	96.81	83.19	44.70	1.21492	0.09244
$RH_2C_bC_a(O)-NH_2$ ($C=O$ (ii)) ($C-N$ (ii))	N	-0.82688	0	0	0		0.93084	0.86923	-15.65263		100.14	79.86	48.10	1.17127	0.15300
$RH_2C_bC_a(O)-NH_2$ ($C=O$ (ii)) ($C-N$ (ii))	C_a	-0.82688	-1.34946	-0.92918	0	-154.72121	0.91771	0.75878	-17.93127	-17.74041	90.51	89.49	41.30	1.31755	0.00672
$HC_a(NH_2)=O$ ($C=O$ (i))	O	-1.79278	0	0	0		1.00000	0.81871	-16.61853		137.10	42.90	65.45	0.53635	0.59978
$HC_a(NH_2)=O$ ($C=O$ (i))	C_a	-1.79278	--0.82688	0	0	-154.23535	0.91771	0.77991	-17.44541	-17.25455	135.44	44.56	63.28	0.58044	0.55569
$RC_bH_2C_a(NH_2)=O$ ($C=O$ (ii))	O	-1.34946	0	0	0		1.00000	0.84115	-16.17521		137.27	42.73	66.31	0.52193	0.61784
$RC_bH_2C_a(NH_2)=O$ ($C=O$ (ii))	C_a	-1.34946	-0.82688	-0.92918	0	-154.72121	0.91771	0.75878	-17.93127	-17.74041	133.67	46.33	61.70	0.61582	0.52395
$H-C(O)NH_2$ (CH (i))	C	-1.79278	-0.82688	0	0	-154.23535	0.91771	0.77991	-17.44541	-17.25455	62.39	117.61	32.13	1.41810	0.36148
$RH_2C_b-C_a(O)NH_2$	C_a	-0.92918	-1.34946	-0.82688	0	-154.72121	0.91771	0.75878	-17.93127	-17.74041	57.02	122.98	25.76	1.84386	0.41299
$H_3C_b-C_a(O)NH_2$	C_b	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	72.27	107.73	34.17	1.69388	0.26301
$RH_2C_cH_2C_b-C_a(O)NH_2$	C_b	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	65.99	114.01	30.58	1.76270	0.33183
$C-H$ (CH_3)	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H$ (CH_2)	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H$ (CH) (ii)	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ ($C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ ($C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.114. The energy parameters (eV) of functional groups of alkyl amides.

Parameters	$C-H$ (i) Group	$C-C(O)$ Group	$C=O$ (i) Group	$C=O$ (ii) Group	$C-N$ (i) Group	$C-N$ (ii) Group	NH_2 Group	CH_3 Group	CH_2 Group	$C-H$ (ii) Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	1	2	2	1	1	2	3	2	1	1	1	1	1	1	1
n_2	0	0	0	0	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
C_1	0.75	0.5	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	0.93613	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	0.75	1	1	1	1	1	1	1	1	1
c_2	0.91771	0.91771	0.85395	0.85395	0.91140	0.91140	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	2	2	0	0	0	0	1	1	0	0	0	1	1	0
c_4	1	2	4	4	2	2	1	1	1	1	2	2	2	2	2	2
c_5	1	0	0	0	0	0	2	3	2	1	0	0	0	0	0	0
C_{1o}	0.75	1	0.5	0.5	0.5	0.5	1.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$V_e\ (eV)$	-35.12015	-30.19634	-112.61934	-111.25473	-38.24008	-36.88558	-78.77719	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_p\ (eV)$	12.87680	9.50874	23.95107	23.87467	10.40705	10.27417	28.03446	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
$T\ (eV)$	10.48582	7.37432	43.62389	42.82081	11.18655	10.51650	29.77286	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$V_m\ (eV)$	-5.24291	-3.68716	-21.81195	-21.41040	-5.59327	-5.25825	-14.88643	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(_{AO/HO})\ (eV)$	-14.63489	-14.63489	0	0	-14.63489	-14.63489	-14.53414	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(_{AO/HO})\ (eV)$	0	0	-3.58557	-2.69893	-5.23932	-4.35268	-1.65376	0	0	0	0	0	0	0	0	0
$E_T(_{AO/HO})\ (eV)$	-14.63489	-14.63489	3.58557	2.69893	-9.39557	-10.28221	-12.88038	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E(_{n,AO/HO})\ (eV)$	0	0	0	0	0	0	-14.53414	0	0	0	0	0	0	0	0	0
$E_T(_{H_2MO})\ (eV)$	-31.63533	-31.63534	-63.27075	-63.27074	-31.63533	-31.63537	-48.73668	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom, msp^3.AO)\ (eV)$	0	-1.85836	-3.58557	-2.69893	-1.65376	-1.65376	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(_{MO})\ (eV)$	-31.63537	-33.49373	-66.85630	-65.96966	-33.28912	-33.28912	-48.73660	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\ (10^{15}\ rad/s)$	24.1759	14.1117	60.9581	59.4034	13.0822	12.5874	59.4067	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_K\ (eV)$	15.91299	9.28860	40.12366	39.10034	8.61093	8.28526	39.10250	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D\ (eV)$	-0.24966	-0.20195	-0.41891	-0.40804	-0.19325	-0.18957	-0.39136	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}\ (eV)$	0.35532 (Eq. (13.458))	0.14655 [28]	0.21747 [32]	0.21077 [12]	0.17358 [33]	0.17358 [33]	0.40929 [22]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}\ (eV)$	-0.07200	-0.12867	-0.31017	-0.30266	-0.10647	-0.10278	-0.18672	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{mag}\ (eV)$	0.14803	0.14803	0.11441	0.11441	0.14803	0.14803	0.14185	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(_{Group})\ (eV)$	-31.70737	-33.62241	-67.47664	-66.57498	-33.39559	-33.39190	-49.11003	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(_{c_4\ AO/HO})\ (eV)$	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.53414	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(_{c_5\ AO/HO})\ (eV)$	-13.59844	0	0	0	0	0	-13.59844	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(_{Group})\ (eV)$	3.47404	4.35263	8.70826	7.80660	4.12581	4.12212	7.37901	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.115. The total bond energies of alkyl amides calculated using the functional group composition and the energies of Table 15.114 compared to the experimental values [3].

Formula	Name	$C-H$ (i) Group	$C-C(O)$ Group	$C=O$ (i) Group	$C=O$ (ii) Group	$C-N$ (i) Group	$C-N$ (ii) Group	NH_2 Group	CH_3	CH_2	CH (ii)	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_3NO	Formamide	1	0	1	0	1	0	1	0	0	0	0	0	0	0	0	0	23.68712	23.697	0.00041
C_2H_5NO	Acetamide	0	1	0	1	0	1	1	1	0	0	0	0	0	0	0	0	36.15222	36.103	-0.00135
C_3H_7NO	Propanamide	0	1	0	1	0	1	1	1	1	0	1	0	0	0	0	0	48.30992	48.264	-0.00094
C_4H_9NO	Butanamide	0	1	0	1	0	1	1	1	2	0	2	0	0	0	0	0	60.46762	60.449	-0.00030
C_4H_9NO	2-Methylpropanamide	0	0	0	1	0	1	1	2	0	1	0	3	0	0	0	0	60.51509	60.455	-0.00099
$C_5H_{11}NO$	Pentanamide	0	1	0	1	0	1	1	1	3	0	3	0	0	0	0	0	72.65232	72.481	-0.00200
$C_5H_{11}NO$	2,2-Dimethylpropanamide	0	0	0	1	0	1	1	3	0	0	0	0	3	0	0	0	72.67890	72.718	0.00054
$C_6H_{13}NO$	Hexanamide	0	1	0	1	0	1	1	1	4	0	4	0	0	0	0	0	84.78302	84.780	-0.00004
$C_8H_{17}NO$	Octanamide	0	1	0	1	0	1	1	1	6	0	6	0	0	0	0	0	109.09842	109.071	-0.00025

Table 15.116. The bond angle parameters of alkyl amides and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom, msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HNH$	1.94130	1.94130	3.1464	-14.53414	N	H	H	0.93613 Eq. (15.62))	1	1	1	0.75	1.06823	0				108.27	
$\angle C_aNH$ $(CH\ (i);\ C_a=O\ (i))$	2.61473	1.94130	3.9328	-14.53414 N	N	-14.82575 C_a	1	0.93613 (Eq. (15.62))	0.91771	0.75	1	0.75	0.98033	0				118.61	119.2 (formamide)
$\angle HC_aN$ $(CH\ (i);\ C_a=O\ (i))$	2.11323	2.61473	4.0825	-14.82575 C_a	1	-14.53414 N	N	0.91771	0.93613 (Eq. (15.62))	0.75	1	0.75	1.02006	0				119.04	
$\angle HC_aO_a$ $(CH\ (i))$	2.11323	2.27227	3.7238	-14.82575 C_a	1	-13.61806	O	0.91771	0.85395 (Eq. (15.114))	0.75	1	0.75	0.93052	0				116.18	
$\angle OC_aN$ $(C_a=O\ (i))$	2.27227	2.61473	4.3359	16.17521 O	12	-16.37720 N	17	0.84115	0.83078	1	1	1	0.83596	-1.44915				124.91	125.0 (formamide)
$\angle C_bC_aN$ $(C_a=O\ (ii))$	2.86175	2.64855	4.6904	-15.75493 C_b	7	-14.53414 N	N	0.86359	0.91140 (Eq. (15.116))	1	1	1	0.88749	-1.44915				116.63	115.1 (acetamide)
$\angle C_bC_aO$ $(C_a=O\ (ii))$	2.86175	2.27954	4.5607	-16.68411	24	-13.61806	O	0.81549	0.85395 (Eq. (15.114))	1	1	1	0.83472	-1.65376				124.63	
$\angle OC_aN$ $(C_a=O\ (ii))$	2.27954	2.64855	4.3128	16.17521 O	12	-16.37720 N	17	0.84115	0.83078	1	1	1	0.83596	-1.44915				121.95	122.0 (acetamide)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	108.5 (acetone)
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

N-ALKYL AND N,N-DIALKYL-AMIDES ($C_nH_{2n+1}NO,\ n=2,3,4,5...\infty$)

The N-alkyl and N,N-dialkyl amides, $C_nH_{2n+1}NO$, comprise a $C=O$ functional group, and the single bond of carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. Formamide has a $HC=O$ moiety that comprises a more stable $C=O$ functional group and a CH functional group that is equivalent to that of the iso-CH group of branched-chain-alkyl portion of the N-alkyl or N,N-dialkyl amide. All amides further comprise a $C-N(R_1)R_2$ moiety that comprises two types of $C-N$ functional groups, one for formamide and the other for alkyl amides ($RC(O)N(R_1)R_2$ where R is alkyl). The N or N,N-dialkyl moiety comprises three additional groups depending on the alkyl substitution of the nitrogen. In the case of a single methyl or alkyl substitution, the $NH-C$ bond and NH are functional groups, and the $N-C$ bond of a di-substituted nitrogen is the third.

The alkyl portion of the N-alkyl or N,N-dialkyl amide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in N-alkyl or N,N-dialkyl amides are equivalent to those in branched-chain alkanes.

The NH functional group was solved in the Hydrogen Nitride (NH) section except that the energy of the $N-H$ MO is matched to the nitrogen-atom contribution to $\Delta E_{H_2MO}(AO/HO)$ and $E_T(atom-atom,msp^3.AO)$ of the $C-N$ group. The $C-C(O)$ group, both N-alkyl or N,N-dialkyl amide $C=O$ groups, and both $C-N$ groups are equivalent to those given in the Amides section.

As in the case of primary amines, each $N-C$ group is solved by hybridizing the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the N AO to form a MO permits each participating orbital to decrease in radius and energy. To meet the equipotential condition of the union of the

$N-C$ H_2-type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor c_2 of Eq. (15.52) for the $N-C$-bond MO given by Eq. (15.114) is $c_2(C2sp^3HO\ to\ N)=0.91140$.

$E_T(atom-atom,msp^3.AO)$ of the N-substituted amide $C-C(O)$ group is the same as alkanes, aldehydes, carboxylic acids, carboxylic acid esters, and amides, $-1.85836\ eV$, where both energy contributions are given by Eq. (14.513). Also, as in the case of aldehydes, $C_{1o}=2C_1$ in Eq. (15.52).

$E_T(atom-atom,msp^3.AO)$ (Eq. (15.52)) of the $C=O$ group of N-substituted alky amides and the $C=O$ group of N-substituted formamide are equivalent to those of the corresponding carboxylic acids, carboxylic esters, and amides. The values given in the Carboxylic Acids section are $-2.69893\ eV$ and $-3.58557\ eV$, respectively.

$E_T(atom-atom,msp^3.AO)$ of both $C-N$ functional groups are the same as those of the corresponding groups of amides, $-1.65376\ eV$. $E_T(atom-atom,msp^3.AO)$ of the singly-substituted $NH-C$-bond MO in Eq. (15.52) due to the charge donation from the N and C atoms to the MO is $-0.92918\ eV$. It is equivalent to that of tertiary amines and matches the energy of the $NH-C$ group to that of the $C-N$ group wherein $E_T(atom-atom,msp^3.AO)$ of the latter is a linear combination of $-0.92918\ eV$ (Eq. (14.513)) and $-0.72457\ eV$ (Eq. (14.151)). $E_T(atom-atom,msp^3.AO)$ of the doubly-substituted $N-C$-bond MO is $-0.72457\ eV$. It is equivalent to that of the contribution of each atom of a primary amine and also matches the energy of the $N-C$ group to that of the $C-N$ group by matching one of the components of $E_T(atom-atom,msp^3.AO)$ of the latter.

The symbols of the functional groups of N-alkyl and N,N-dialkyl amides are given in Table 15.117. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of N-alkyl and N,N-dialkyl amides are given in Tables 15.118, 15.119, and 15.120, respectively. The total energy of each N-alkyl or N,N-dialkyl amide given in Table 15.121 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.120 corresponding to functional-group composition of the molecule. The bond angle parameters of N-alkyl and N,N-dialkyl amides determined using Eqs. (15.79-15.108) are given in Table 15.122.

Table 15.117. The symbols of functional groups of N-alkyl and N,N-dialkyl amides.

Functional Group	Group Symbol
C-C(O)	$C-C(O)$
C=O (N-alkyl and N,N-dialkyl formamide)	$C=O$ (i)
C=O (N-alkyl and N,N-dialkyl amide)	$C=O$ (ii)
(O)C-N (N-alkyl and N,N-dialkyl formamide)	$C-N$ (i)
(O)C-N (N-alkyl and N,N-dialkyl amide)	$C-N$ (ii)
NH group	NH
N-C (N-alkyl)	$N-C$ (i)
N-C (N,N,-dialkyl)	$N-C$ (ii)
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH (alkyl) group	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.118. The geometrical bond parameters of N-alkyl and N,N-dialkyl amides and experimental values [1]

Parameter	$C-C(O)$ Group	$C=O$ (i) Group	$C=O$ (ii) Group	$C-N$ (i) Group	$C-N$ (ii) Group	NH Group	$N-C$ (i) Group	$N-C$ (ii) Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	2.04740	1.290799	1.29907	1.70920	1.75370	1.28620	1.96313	1.97794	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.43087	1.13613	1.13977	1.30736	1.32427	0.95706	1.40112	1.40639	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ ($\mathring{A}$)	1.51437	1.20243	1.20628	1.38365	1.40155	1.01291	1.48288	1.48846	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length ($\mathring{A}$)	1.520 (N-methyl-acetamide)	1.212 (formamide)	1.225 (N-methyl-acetamide)	1.368 (formamide)	1.380 (acetamide)		1.469 (N-methyl-acetamide)		1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	1.46439	0.61267	0.62331	1.10098	1.14968	0.85927	1.37505	1.39079	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.69887	0.88018	0.87737	0.76490	0.75513	0.74410	0.71372	0.71104	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.119. The MO to HO intercept geometrical bond parameters of N-alkyl and N,N-dialkyl amides. R,R',R'' are H, methyl, or alkyl groups. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_o)	r_{final} (a_o)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_o)	d_2 (a_o)
$R'C_a(O)N(C_bR)-H$ $(C=O$ (i) and (ii)) $(C-N$ (i) and (ii))	N	-0.82688	-0.46459	0	0		0.93084	0.84418	-16.11722		115.47	64.53	62.49	0.59403	0.36303
$RC_a(O)N(H)-C_bH_3$ $(C=O$ (i) and (ii)) $(C-N$ (i) and (ii)) $(N-C$ (i))	N	-0.82688	-0.46459	0	0		0.93084	0.84418	-16.11722		78.61	101.39	37.00	1.56779	0.16667
$RC_a(O)N(H)-C_bH_3$ $(C=O$ (i) and (ii)) $(C-N$ (i) and (ii)) $(N-C$ (i))	C_b	-0.46459	0	0	0	-152.08028	0.91771	0.88983	-15.29034	-15.09948	83.37	96.63	40.00	1.50383	0.10271
$R'C_a(O)N(H)-C_bH_2C_cH_2R$ $(C=O$ (i) and (ii)) $(C-N$ (i) and (ii)) $(N-C$ (i))	N	-0.82688	-0.46459	0	0		0.93084	0.84418	-16.11722		78.61	101.39	37.00	1.56779	0.16667
$R'C_a(O)N(H)-C_bH_2C_cH_2R$ $(C=O$ (i) and (ii)) $(C-N$ (i) and (ii)) $(N-C$ (i))	C_b	-0.46459	-0.92918	0	0	-153.00946	0.91771	0.83885	-16.21952	-16.02866	78.02	101.39	36.64	1.57525	0.17413
$R'C_a(O)N(C_cH_3)-C_bH_3$ $(C=O$ (i) and (ii)) $(C-N$ (i) and (ii)) $(N-C$ (ii))	N	-0.82688	-0.36229	-0.36229	0		0.93084	0.83078	-16.37720		75.57	104.43	35.35	1.61336	0.20697
$R'C_a(O)N(C_cH_3)-C_bH_3$ $(C=O$ (i) and (ii)) $(C-N$ (i) and (ii)) $(N-C$ (ii))	C_b	-0.36229	0	0	0	-151.97798	0.91771	0.89582	-15.18804	-14.99717	82.59	97.41	39.70	1.52188	0.11549
$R'C_a(O)N(C_cH_2C_dH_2R)-C_bH_3$ $(C=O$ (i) and (ii)) $(C-N$ (i) and (ii)) $(N-C$ (ii))	N	-0.82688	-0.36229	-0.36229	0		0.93084	0.83078	-16.37720		75.57	104.43	35.35	1.61336	0.20697
$R'C_a(O)N(C_cH_2C_dH_2R)-C_bH_3$ $(C=O$ (i) and (ii)) $(C-N$ (i) and (ii)) $(N-C$ (ii))	C_c	-0.36229	0	0	0	-151.97798	0.91771	0.89582	-15.18804	-14.99717	82.59	97.41	39.70	1.52188	0.11549
$R''C_a(O)N(R')-C_bH_2C_cH_2R$ $(C=O$ (i) and (ii)) $(C-N$ (i) and (ii)) $(N-C$ (ii))	N	-0.82688	-0.36229	-0.36229	0		0.93084	0.83078	-16.37720		75.57	104.43	35.35	1.61336	0.20697
$R''C_a(O)N(R')-C_bH_2C_cH_2R$ $(C=O$ (i) and (ii)) $(C-N$ (i) and (ii)) $(N-C$ (ii))	C_b	-0.36229	-0.92918	0	0	-152.90716	0.91771	0.84418	-16.11722	-15.92636	77.12	102.88	36.28	1.59451	0.18812
$HC_a(O)-N(H)R$ $(C=O$ (i)) $(C-N$ (i)) $(N-C$ (i)) $R=methyl\ or\ alkyl$	N	-0.82688	-0.46459	0	0		0.93084	0.84418	-16.11722		102.07	77.93	48.57	1.13090	0.17647
$HC_a(O)-N(H)R$ $(C=O$ (i)) $(C-N$ (i)) $(N-C$ (i)) $R=methyl\ or\ alkyl$	C_a	-0.82688	-1.79278	0	0	-154.23535	0.91771	0.77991	-17.44541	-17.25455	96.81	83.19	44.70	1.21492	0.09244
$HC_a(O)-N(R')R$ $(C=O$ (i)) $(C-N$ (i)) $(N-C$ (ii)) $R,R'=methyl\ or\ alkyl$	N	-0.82688	-0.36229	-0.36229	0		0.93084	0.83078	-16.37720		101.03	78.97	47.79	1.14842	0.15895
$HC_a(O)-N(R')R$ $(C=O$ (i)) $(C-N$ (i)) $(N-C$ (ii))	C_a	-0.82688	-1.79278	0	0	-154.23535	0.91771	0.77991	-17.44541	-17.25455	96.81	83.19	44.70	1.21492	0.09244

$R,R'=$ *methyl or alkyl*															
$R'H_2C_bC_a(O)-N(H)R$ $(C=O$ (ii)) $(C-N$ (ii)) $(N-C$ (i)) $R=$ *methyl or alkyl*	N	-0.82688	-0.46459	0	0		0.93084	0.84418	-16.11722		98.16	81.84	46.62	1.20446	0.11982
$R'H_2C_bC_a(O)-N(H)R$ $(C=O$ (ii)) $(C-N$ (ii)) $(N-C$ (i)) $R=$ *methyl or alkyl*	C'_a	-0.82688	-1.34946	-0.92918	0	-154.72121	0.91771	0.75878	-17.93127	-17.74041	90.51	89.49	41.30	1.31755	0.00672
$R''H_2C_bC_a(O)-N(R')R$ $(C=O$ (ii)) $(C-N$ (ii)) $(N-C$ (ii)) $R,R'=$ *methyl or alkyl*	N	-0.82688	-0.36229	-0.36229	0		0.93084	0.83078	-16.37720		97.06	82.94	45.82	1.22220	0.10207
$R''H_2C_bC_a(O)-N(R')R$ $(C=O$ (ii)) $(C-N$ (ii)) $(N-C$ (ii)) $R,R'=$ *methyl or alkyl*	C'_a	-0.82688	-1.34946	-0.92918	0	-154.72121	0.91771	0.75878	-17.93127	-17.74041	90.51	89.49	41.30	1.31755	0.00672
$HC_a(N(R'')R')=O$ $(C=O$ (i)) $R',R''=H,$ *methyl, or alkyl*	O	-1.79278	0	0	0		1.00000	0.81871	-16.61853		137.10	42.90	65.45	0.53635	0.59978
$HC_a(N(R'')R')=O$ $(C=O$ (i)) $R',R''=H,$ *methyl, or alkyl*	C'_a	-1.79278	-0.82688	0	0	-154.23535	0.91771	0.77991	-17.44541	-17.25455	135.44	44.56	63.28	0.58044	0.55569
$RC_bH_2C_a(N(R'')R')=O$ $(C=O$ (ii)) $R',R''=H,$ *methyl, or alkyl*	O	-1.34946	0	0	0		1.00000	0.84115	-16.17521		137.27	42.73	66.31	0.52193	0.61784
$RC_bH_2C_a(N(R'')R')=O$ $(C=O$ (ii)) $R',R''=H,$ *methyl, or alkyl*	C'_a	-1.34946	-0.82688	-0.92918	0	-154.72121	0.91771	0.75878	-17.93127	-17.74041	133.67	46.33	61.70	0.61582	0.52395
$H-C'(O)N(R'')R'$ $R',R''=H,$ *methyl, or alkyl*	C'	-1.79278	-0.82688	0	0	-154.23535	0.91771	0.77991	-17.44541	-17.25455	62.39	117.61	32.13	1.41810	0.36148
$RH_2C_b-C_a(O)N(R'')R'$ $R',R''=H,$ *methyl, or alkyl*	C'_a	-0.92918	-1.34946	-0.82688	0	-154.72121	0.91771	0.75878	-17.93127	-17.74041	57.02	122.98	25.76	1.84386	0.41299
$H_3C_b-C_a(O)N(R'')R'$ $R',R''=H,$ *methyl, or alkyl*	C'_b	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	72.27	107.73	34.17	1.69388	0.26301
$RH_2C_cH_2C_b-C_a(O)N(R'')R'$ $R',R''=H,$ *methyl, or alkyl*	C'_b	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	65.99	114.01	30.58	1.76270	0.33183
$C'-H\ (C'H_3)$	C'	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C'-H\ (C'H_2)$	C'	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C'-H\ (C'H)$ (ii)	C'	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C'_aC'_bH_2CH_2-$ $(C'-C'$ (a))	C'_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C'_aC'_bH_2CH_2-$ $(C'-C'$ (a))	C'_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C'_aC'_b(H_2C'_c-R')HCH_2-$ $(C'-C'$ (b))	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C'_a(R'-H_2C'_d)C'_b(R''-H_2C'_c)CH_2-$ $(C'-C'$ (c))	C'_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC'_aC'_b(H_2C'_c-R')HCH_2-$ $(C'-C'$ (d))	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC'_a(R'-H_2C'_d)C'_b(R''-H_2C'_c)CH_2-$ $(C'-C'$ (e))	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC'_aC'_b(H_2C'_c-R')HCH_2-$ $(C'-C'$ (f))	C'_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC'_a(R'-H_2C'_d)C'_b(R''-H_2C'_c)CH_2-$ $(C'-C'$ (f))	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.120. The energy parameters (eV) of functional groups of N-alkyl and N,N-dialkyl amides.

Parameters	$C-C(O)$ Group	$C=O$ (i) Group	$C=O$ (ii) Group	$C-N$ (i) Group	$C-N$ (ii) Group	NH Group	$N-C$ (i)	$N-C$ (ii)	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	2	2	1	1	1	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	0	0	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.5	0.5	0.75	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	0.93613	1	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	0.75	1	1	1	1	1	1	1	1	1	1	1
c_2	0.91771	0.85395	0.85395	0.91140	0.91140	1	0.91140	0.91140	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	2	2	0	0	1	0	0	0	1	1	0	0	0	1	1	0
c_4	2	4	4	2	2	1	2	2	1	1	1	2	2	2	2	2	2
c_5	0	0	0	0	0	1	0	0	3	2	1	0	0	0	0	0	0
C_{1o}	1	0.5	0.5	0.5	0.5	0.75	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
V_e (eV)	-30.19634	-112.61934	-111.25473	-38.24008	-36.88558	-40.92593	-31.67393	-31.36351	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	9.50874	23.95107	23.87467	10.40705	10.27417	14.21618	9.71067	9.67426	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	7.37432	43.62389	42.82081	11.18655	10.51650	15.90963	8.06719	7.92833	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_m (eV)	-3.68716	-21.81195	-21.41040	-5.59327	-5.25825	-7.95482	-4.03359	-3.96416	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(_{AO/HO})$ (eV)	-14.63489	0	0	-14.63489	-14.63489	-14.53414	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(_{AO/HO})$ (eV)	0	-3.58557	-2.69893	-5.23932	-4.35268	-1.65376	-0.92918	-0.72457	0	0	0	0	0	0	0	0	0
$E_T(_{AO/HO})$ (eV)	-14.63489	3.58557	2.69893	-9.39557	-10.28221	-12.88038	-13.70571	-13.91032	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(_{H_2MO})$ (eV)	-31.63534	-63.27075	-63.27074	-31.63533	-31.63537	-31.63531	-31.63537	-31.63540	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom,msp^3.AO)$ (eV)	-1.85836	-3.58557	-2.69893	-1.65376	-1.65376	0	-0.92918	-0.72457	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(_{MO})$ (eV)	-33.49373	-66.85630	-65.96966	-33.28912	-33.28912	-31.63537	-32.56455	-32.35994	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω $(10^{15}$ $rad/s)$	14.1117	60.9581	59.4034	13.0822	12.5874	44.9494	10.6278	10.5087	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	9.28860	40.12366	39.10034	8.61093	8.28526	29.58649	6.99543	6.91703	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D$ (eV)	-0.20195	-0.41891	-0.40804	-0.19325	-0.18957	-0.34043	-0.17039	-0.16837	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}$ (eV)	0.14655 [28]	0.21747 [32]	0.21077 [12]	0.17358 [33]	0.17358 [33]	0.40696 [24]	0.12944 [23]	0.12944 [23]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}$ (eV)	-0.12867	-0.31017	-0.30266	-0.10647	-0.10278	-0.13695	-0.10567	-0.10365	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mag} (eV)	0.14803	0.11441	0.11441	0.14803	0.14803	0.14185	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(_{Group})$ (eV)	-33.62241	-67.47664	-66.57498	-33.39559	-33.39190	-31.77232	-32.67022	-32.46359	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(c_4$ $_{AO/HO})$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.53414	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(c_5$ $_{AO/HO})$ (eV)	0	0	0	0	0	-13.59844	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(_{Group})$ (eV)	4.35263	8.70826	7.80660	4.12581	4.12212	3.49788	3.40044	3.19381	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.121. The total bond energies of N-alkyl and N,N-dialkyl amides calculated using the functional group composition and the energies of Table 15.120 compared to the experimental values [3].

Formula	Name	$C-C(O)$ Group	$C=O$ (i) Group	$C=O$ (ii) Group	$C-N$ (i) Group	$C-N$ (ii) Group	NH Group	$N-C$ (i)	$N-C$ (ii)	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_3H_7NO	N,N-Dimethylformamide	0	1	0	1	0	0	0	2	2	0	1	0	0	0	0	0	0	47.53142	47.574	0.00090
C_4H_9NO	N,N-Dimethylacetamide	0	0	1	0	2	0	0	2	3	0	0	0	0	0	0	0	0	59.91404	59.890	-0.00041
$C_6H_{13}NO$	N-Butylacetamide	1	0	1	0	1	1	1	0	2	3	0	3	0	0	0	0	0	84.63649	84.590	-0.00055

Table 15.122. The bond angle parameters of N-alkyl and N,N-dialkyl amides and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle OC_aN$ $(C_n=O$ (ii))	2.27954	2.64855	4.3243	16.17521 O	12	-16.11722 N	11	0.84115	0.84418	1	1	1	0.84266	-1.44915				122.51	121.8 (N-methylacetamide)
$\angle C_bC_aN$ $(C_n=O$ (ii))	2.86175	2.64855	4.6904	-15.75493 C_b	7	-14.53414 N	N	0.86359	0.91140 (Eq. (15.116))	1	1	1	0.88749	-1.44915				116.63	114.1 (N-methylacetamide)
$\angle C_bC_aO$ $(C_n=O$ (ii))	2.86175	2.27954	4.5607	-16.68411	24	-13.61806	O	0.81549	0.85395 (Eq. (15.114))	1	1	1	0.83472	-1.65376				124.63	
$\angle C_aNC_c$ $(C_n=O$ (ii))	2.64855	2.80224	4.6904	-17.93127 C_a	48	-16.21952 C_c	14	0.75878	0.83885	1	1	1	0.79881	-1.85836				118.72	119.7 (N-methylacetamide)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	108.5 (acetone)
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

UREA (CH_4N_2O)

Urea, CH_4N_2O, comprises a $C=O$ functional group and two $C-NH_2$ moieties that each comprise a NH_2 functional group and a $C-N$ functional group. The $C=O$ group is equivalent to that given for formamide in the Amides section except that the energy terms due to oscillation in the transition state are matched to that of urea. The NH_2 and $C-N$ functional groups are also equivalent to those given in the Amides section. $E_T\left(atom-atom,msp^3.AO\right)$ (Eq. (15.52)) of the $C=O$ and $C-N$ groups are equivalent to those of formamide. The values given in the Amides section are $-3.58557\ eV$, and $-1.65376\ eV$, respectively.

The symbols of the functional groups of urea are given in Table 15.123. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of urea are given in Tables 15.124, 15.125, and 15.126, respectively. The total energy of urea given in Table 15.127 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.126 corresponding to functional-group composition of the molecule. The bond angle parameters of urea determined using Eqs. (15.79-15.108) are given in Table 15.128.

Table 15.123. The symbols of functional groups of urea.

Functional Group	Group Symbol
C=O (urea)	$C=O$
(O)C-N (urea)	$C-N$
NH_2 group	NH_2

Table 15.124. The geometrical bond parameters of urea and experimental values [1].

Parameter	$C=O$ Group	$C-N$ Group	NH_2 Group
a (a_0)	1.290799	1.70920	1.32297
c' (a_0)	1.13613	1.30736	0.97065
Bond Length $2c'$ $(Å)$	1.20243	1.38365	1.02729
Exp. Bond Length $(Å)$	1.212 (formamide)	1.368 (formamide)	1.027 (formamide) 1.022 (acetamide)
b,c (a_0)	0.61267	1.10098	0.89894
e	0.88018	0.76490	0.73369

Table 15.125. The MO to HO intercept geometrical bond parameters of urea. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' $(°)$	θ_1 $(°)$	θ_2 $(°)$	d_1 (a_0)	d_2 (a_0)
$H_2NC(O)N(H)-H$	N	-0.82688	0	0	0		0.93084	0.86923	-15.65263		113.90	66.10	62.13	0.61843	0.35222
$H_2NC(O)-NH_2$	N	-0.82688	0	0	0		0.93084	0.86923	-15.65263		103.93	76.07	50.02	1.09814	0.20922
$H_2NC(O)-NH_2$	C'	-0.82688	-1.79278	-0.82688	0	-155.06223	0.91771	0.74461	-18.27229	-18.08143	93.56	86.44	42.45	1.26106	0.04630
$H_2NC_a(NH_2)=O$	O	-1.79278	0	0	0		1.00000	0.81871	-16.61853		137.10	42.90	65.45	0.53635	0.59978
$H_2NC_a(NH_2)=O$	C'	-1.79278	-0.82688	-0.82688	0	-155.06223	0.91771	0.74461	-18.27229	-18.08143	133.82	46.18	61.27	0.62054	0.51559

Table 15.126. The energy parameters (eV) of functional groups of urea.

Parameters	$C=O$ Group	$C-N$ Group	NH_2 Group
n_1	2	1	2
n_2	0	0	0
n_3	0	0	1
C_1	0.5	0.5	0.75
C_2	1	1	0.93613
c_1	1	1	0.75
c_2	0.85395	0.91140	1
c_3	2	0	0
c_4	4	2	1
c_5	0	0	2
C_{1o}	0.5	0.5	1.5
C_{2o}	1	1	1
$V_e\ (eV)$	-112.61934	-38.24008	-78.77719
$V_p\ (eV)$	23.95107	10.40705	28.03446
$T\ (eV)$	43.62389	11.18655	29.77286
$V_m\ (eV)$	-21.81195	-5.59327	-14.88643
$E(_{AO/HO})\ (eV)$	0	-14.63489	-14.53414
$\Delta E_{H_2MO}(_{AO/HO})\ (eV)$	-3.58557	-5.23932	-1.65376
$E_T(_{AO/HO})\ (eV)$	3.58557	-9.39557	-12.88038
$E(_{n_3\ AO/HO})\ (eV)$	0	0	-14.53414
$E_T(_{H_2MO})\ (eV)$	-63.27075	-31.63533	-48.73668
$E_T\left(atom-atom, msp^3.AO\right)\ (eV)$	-3.58557	-1.65376	0
$E_T(_{MO})\ (eV)$	-66.85630	-33.28912	-48.73660
$\omega\ \left(10^{15}\ rad/s\right)$	19.9334	13.0822	59.4067
$E_K\ (eV)$	13.12053	8.61093	39.10250
$\bar{E}_D\ (eV)$	-0.23955	-0.19325	-0.39136
$\bar{E}_{Kvib}\ (eV)$	0.21747 [32]	0.17358 [33]	0.40929 [22]
$\bar{E}_{osc}\ (eV)$	-0.13081	-0.10647	-0.18672
$E_{mag}\ (eV)$	0.11441	0.14803	0.14185
$E_T(_{Group})\ (eV)$	-67.11793	-33.39559	-49.11003
$E_{initial}(_{c_4\ AO/HO})\ (eV)$	-14.63489	-14.63489	-14.53414
$E_{initial}(_{c_5\ AO/HO})\ (eV)$	0	0	-13.59844
$E_D(_{Group})\ (eV)$	8.34955	4.12581	7.37901

Table 15.127. The total bond energies of urea calculated using the functional group composition and the energies of Table 15.126 compared to the experimental values [3].

Formula	Name	$C=O$ Group	$C-N$ Group	NH_2 Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_4N_2O	Urea	1	2	2	31.35919	31.393	0.00108

Table 15.128. The bond angle parameters of urea and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HNH$	1.94130	1.94130	3.1464	-14.53414	N	H	H	0.93613 Eq. (15.62))	1	1	1	0.75	1.06823	0				108.27	
$\angle C'_a NH$	2.61473	1.94130	3.9328	-14.53414 N	N	-14.82575 C'_a	1	0.93613 (Eq. (15.62))	0.91771	0.75	1	0.75	0.98033	0				118.61	119.2 (formamide)
$\angle OC'_a N$	2.27227	2.61473	4.3359	16.17521 O	12	-16.37720 N	17	0.84115	0.83078	1	1	1	0.83596	-1.44915				124.91	125.0 (formamide)

CARBOXYLIC ACID HALIDES ($C_nH_{2n-1}OX,\ X = F, Cl, Br, I;\ n = 1,2,3,4,5...\infty$)

The alkyl carboxylic acid halides, $C_nH_{2n-1}OX$, comprise a $C=O$ functional group, and the single bond of carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. All carboxylic acid halides further comprise a $C-X$ functional group where X is a halogen atom. The alkyl portion of the alkyl carboxylic acid halide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acids are equivalent to those in branched-chain alkanes.

The alkyl carboxylic acid halide $C=O$ and $C-C(O)$ groups are equivalent to those given in the Aldehydes section and the Ketones section, respectively. The values of $E_T(atom-atom, msp^3.AO)$ given in these sections are $-2.69893\ eV$ and $-1.44915\ eV$, respectively.

As in the case of alkyl halides, each $(O)C-X$ group is solved by hybridizing the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the X AO to form a MO permits each participating orbital to decrease in radius and energy. For example, to meet the equipotential condition of the union of the $(O)C-Cl$ H_2-type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor C_2 of Eq. (15.52) for the $(O)C-Cl$-bond MO given by Eq. (15.111) is $C_2(C2sp^3HO\ to\ Cl) = 0.81317$. The solution is equivalent to that of the alkyl chloride bond except that the energy parameters corresponding to oscillation in the transition state are matched to those of a carboxylic acid chloride.

As in the case with the $C-Cl$ group of alkyl chlorides, $E_T(atom-atom, msp^3.AO)$ of the $(O)C-Cl$-bond MO in Eq. (15.52) of alky carboxylic acid chlorides due to the charge donation from the C and Cl atoms to the MO is $-1.44915\ eV$ where both energy contributions

are given by Eq. (14.511). This matches the energy of the $C-C(O)$ functional group with that of the $(O)C-Cl$ group within the carboxylic acid chloride molecule.

The symbols of the functional groups of alkyl carboxylic acid chlorides are given in Table 15.129. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl carboxylic acid chlorides are given in Tables 15.130, 15.131, and 15.132, respectively. The total energy of each alkyl carboxylic acid chloride given in Table 15.133 was calculated as the sum over the integer multiple of each $E_D(_{Group})$ of Table 15.132 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl carboxylic acid chlorides determined using Eqs. (15.79-15.108) are given in Table 15.134.

Table 15.129. The symbols of functional groups of alkyl carboxylic acid chlorides.

Functional Group	Group Symbol
C-C(O)	$C-C(O)$
C=O (alkyl carboxylic acid chloride)	$C=O$
(O)C-Cl	$C-Cl$
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH (alkyl) group	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.130. The geometrical bond parameters of alkyl carboxylic acid chlorides and experimental values [1].

Parameter	$C-C(O)$ Group	$C=O$ Group	$C-Cl$ Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	2.04740	1.29907	2.32621	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.43087	1.13977	1.69136	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (Å)$	1.51437	1.20628	1.79005	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(Å)$	1.520 (acetone) 1.518 (2-butanone)	1.187 (acetyl chloride) 1.214 (acetic acid)	1.798 (acetyl chloride)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	1.46439	0.62331	1.59705	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.69887	0.87737	0.72709	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.131. The MO to HO intercept geometrical bond parameters of alkyl carboxylic acid chlorides. R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$H_3C_bC_a(O)-Cl$	Cl	-0.72457	0	0	0		1.05158	0.87495	-15.55033		69.62	110.38	30.90	1.99599	0.30463
$H_3C_bC_a(O)-Cl$	C_a	-1.34946	-0.72457	-0.72457	0	-154.41430	0.91771	0.77199	-17.62436	-17.43350	54.69	125.31	23.23	2.13760	0.44625
$H_3C_bC_a(Cl)=O$	O	-1.34946	0	0	0		1.00000	0.84115	-16.17521		137.27	42.73	66.31	0.52193	0.61784
$H_3C_bC_a(Cl)=O$	C_a	-1.34946	-0.72457	-0.72457	0	-154.41430	0.91771	0.77199	-17.62436	-17.43350	134.28	45.72	62.45	0.60076	0.53901
$H_3C_b-C_a(O)-Cl$	C_a	-0.72457	-1.34946	-0.72457	0	-154.41430	0.91771	0.77199	-17.62436	-17.43350	59.30	120.70	26.96	1.82495	0.39408
$H_3C_b-C_a(O)-Cl$	C_b	-0.72457	0	0	0	-152.34026	0.91771	0.87495	-15.55033	-15.35946	73.62	106.38	34.98	1.67762	0.24675
$C-H\ (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\ (CH)$ (ii)	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.132. The energy parameters (eV) of functional groups of alkyl carboxylic acid chlorides.

Parameters	$C-C(O)$ Group	$C=O$ Group	$C-Cl$ Group	CH_3 Group	CH_2 Group	$C-H$ (ii) Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	2	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	0.81317	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1	1
c_2	0.91771	0.85395	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	2	1	0	1	1	0	0	0	1	1	0
c_4	2	4	2	1	1	1	2	2	2	2	2	2
c_5	0	0	0	3	2	1	0	0	0	0	0	0
C_{1o}	1	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	1	1	0.81317	1	1	1	1	1	1	1	1	1
$V_e\ (eV)$	-30.19634	-111.25473	-29.68411	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_p\ (eV)$	9.50874	23.87467	8.04432	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
$T\ (eV)$	7.37432	42.82081	6.38036	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$V_m\ (eV)$	-3.68716	-21.41040	-3.19018	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(_{AO/HO})\ (eV)$	-14.63489	0	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(_{AO/HO})\ (eV)$	0	-2.69893	-1.44915	0	0	0	0	0	0	0	0	0
$E_T(_{AO/HO})\ (eV)$	-14.63489	2.69893	-13.18574	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(_{H_2MO})\ (eV)$	-31.63534	-63.27074	-31.63536	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T\left(atom-atom,msp^3.AO\right)\ (eV)$	-1.44915	-2.69893	-1.44915	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(_{MO})\ (eV)$	-33.08452	-65.96966	-33.08452	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\ \left(10^{15}\ rad/s\right)$	16.4962	59.4034	7.42995	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_K\ (eV)$	10.85807	39.10034	4.89052	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D\ (eV)$	-0.21568	-0.40804	-0.14475	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}\ (eV)$	0.14655 [28]	0.21077 [12]	0.09063 [34]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}\ (eV)$	-0.14240	-0.30266	-0.09943	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{mag}\ (eV)$	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(_{Group})\ (eV)$	-33.22692	-66.57498	-33.18395	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(c_4\ _{AO/HO})\ (eV)$	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(c_5\ _{AO/HO})\ (eV)$	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(_{Group})\ (eV)$	3.95714	7.80660	3.76614	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.133. The total bond energies of alkyl carboxylic acid chlorides calculated using the functional group composition and the energies of Table 15.102 compared to the experimental values [3].

Formula	Name	$C-C(O)$ Group	$C=O$ Group	$C-Cl$ Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_3ClO	Acetyl chloride	1	1	1	1	0	0	0	0	0	0	0	0	28.02174	27.990	-0.00115

Table 15.134. The bond angle parameters of alkyl carboxylic acid chlorides and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle C'_bC'_aO$	2.86175	2.27954	4.5826	-16.68411	24	-13.61806	O	0.81549	0.85395 (Eq. (15.113))	1	1	1	0.83472	-1.65376				125.70	
$\angle C'_bC'_aCl$	2.86175	3.38271	5.1539	-15.75493 C_b	7	-12.96764 Cl	Cl	0.86359	0.86359	1	0.81317 (Eq. (15.111))	1	0.86359	-0.92918				110.98	111.6 (acetyl chloride)
$\angle OC'_aCl$	2.27954	3.38271	4.9841	-16.68412 O	25	-15.55033 Cl	5	0.81549	0.87495	1	0.81317 (Eq. (15.111))	1	0.84522	-0.92918				122.13	121.2 (acetyl chloride)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	108.6 (acetyl chloride) 108.5 (acetone)
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

CARBOXYLIC ACID ANHYDRIDES ($C_nH_{2n-2}O_3$, $n = 2,3,4,5...\infty$)

The alkyl carboxylic acid anhydrides, $C_nH_{2n-2}O_3$, have two $(O)C-O$ moieties that each comprise $C=O$ and $C-O$ functional groups. The single bond of carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. The alkyl portion of the alkyl carboxylic acid anhydride may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acid anhydrides are equivalent to those in branched-chain alkanes.

The alkyl carboxylic acid anhydride $C=O$ and $C-C(O)$ groups are equivalent to those given in the Carboxylic Acid Esters section and the Ketones section, respectively. The values of $E_T(atom-atom,msp^3.AO)$ given in these sections are $-2.69893\ eV$ and $-1.44915\ eV$, respectively. The $C-O$ group is also equivalent to that given in the Carboxylic Acid Esters section except that $E_T(atom-atom,msp^3.AO)$ is equivalent to that of an alkyl ether as given in the corresponding section and the energy terms due to oscillation in the transition state are matched to that of a carboxylic acid anhydride.

For the $C-O$ group, $E_T(atom-atom,msp^3.AO)$ is $-1.65376\ eV$. It is based on the energy match between the O AO and the $C2sp^3$ HO of each $C-C(O)$ group and is given by the linear combination of $-0.72457\ eV$ (Eq. (14.151)) and $-0.92918\ eV$ (Eq. (14.513)), respectively. This matches $-0.72457\ eV$, the energy contribution of each of the $C2sp^3$ HOs to each $C-C(O)$ functional group, with that of the corresponding energy component of the $C-O$ group and gives a minimum energy within the carboxylic acid anhydride molecule.

The symbols of the functional groups of alkyl carboxylic acid anhydrides are given in Table 15.135. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl carboxylic acid anhydrides are given in Tables 15.136, 15.137, and 15.138, respectively. The total energy of each alkyl

carboxylic acid anhydride given in Table 15.139 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.138 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl carboxylic acid anhydrides determined using Eqs. (15.79-15.108) are given in Table 15.140.

Table 15.135. The symbols of functional groups of alkyl carboxylic acid anhydrides.

Functional Group	Group Symbol
C-C(O)	$C-C(O)$
C=O (alkyl carboxylic acid anhydride)	$C=O$
(O)C-O	$C-O$
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH (alkyl) group	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.136. The geometrical bond parameters of alkyl carboxylic acid anhydrides and experimental values [1].

Parameter	$C-C(O)$ Group	$C=O$ Group	$C-O$ Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	2.04740	1.29907	1.73490	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.43087	1.13977	1.31716	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (Å)$	1.51437	1.20628	1.39402	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(Å)$	1.520 (acetone) 1.518 (2-butanone)	1.214 (acetic acid)	1.393 (avg. methyl formate)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b, c\ (a_0)$	1.46439	0.62331	1.12915	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.69887	0.87737	0.75921	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.137. The MO to HO intercept geometrical bond parameters of alkyl carboxylic acid anhydrides. R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' $(^\circ)$	θ_1 $(^\circ)$	θ_2 $(^\circ)$	d_1 (a_0)	d_2 (a_0)
$RC_bH_2C_a(O)-O_a-C_a(O)C_cH_2R'$	O_a	-0.82688	-0.82688	0	0		1.00000	0.82562	-16.47951		98.32	81.68	46.34	1.19766	0.11949
$RC_bH_2C_a(O)-O_a-C_a(O)C_cH_2R'$	C_a	-0.82688	-1.34946	-0.82688	0	-154.51660	0.91771	0.76753	-17.72667	-17.53580	93.21	86.79	42.74	1.27417	0.04298
$RC_bH_2(R'C_cH_2C_a(O_a)O)C_a=O_a$	O_a	-1.34946	0	0	0		1.00000	0.84115	-16.17521		137.27	42.73	66.31	0.52193	0.61784
$RC_bH_2(R'C_cH_2C_a(O_a)O)C_a=O_a$	C_a	-1.34946	-0.72457	-0.82688	0	-154.51660	0.91771	0.76753	-17.72667	-17.53580	134.08	45.92	62.20	0.60583	0.53394
$RH_2C_b-C_a(O)OC_a(O)C_cH_2R'$	C_a	-0.72457	-1.34946	-0.82688	0	-154.51660	0.91771	0.76753	-17.72667	-17.53580	58.55	121.45	26.56	1.83133	0.40045
$H_3C_b-C_a(O)OC_a(O)C_cH_2R'$	C_b	-0.72457	0	0	0	-152.34026	0.91771	0.87495	-15.55033	-15.35946	73.62	106.38	34.98	1.67762	0.24675
$RH_2C_b-C_a(O)OC_a(O)C_cH_2R'$ $R=alkyl$	C_b	-0.72457	-0.92918	0	0	-153.26945	0.91771	0.82562	-16.47951	-16.28865	67.40	112.60	31.36	1.74821	0.31734
$C-H\ (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\ (CH)$ (ii)	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_b	-0.92918	-0.92918	0	0-	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_e)CH_2-$ $(C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a(R'-H_2C_d)C_b(R''-H_2C_e)CH_2-$ $(C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a(R'-H_2C_d)C_b(R''-H_2C_e)CH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.138. The energy parameters (eV) of functional groups of alkyl carboxylic acid anhydrides.

Parameters	$C-C(O)$ Group	$C=O$ Group	$C-O$ Group	CH_3 Group	CH_2 Group	$C-H$ (ii) Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	2	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1	1
c_2	0.91771	0.85395	0.85395	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	2	0	0	1	1	0	0	0	1	1	0
c_4	2	4	2	1	1	1	2	2	2	2	2	2
c_5	0	0	0	3	2	1	0	0	0	0	0	0
C_{1o}	1	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	1	1	1	1	1	1	1	1	1	1	1	1
V_e (eV)	-30.19634	-111.25473	-35.08488	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	9.50874	23.87467	10.32968	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	7.37432	42.82081	10.11150	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_m (eV)	-3.68716	-21.41040	-5.05575	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(_{AO/HO})$ (eV)	-14.63489	0	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(_{AO/HO})$ (eV)	0	-2.69893	-2.69893	0	0	0	0	0	0	0	0	0
$E_T(_{AO/HO})$ (eV)	-14.63489	2.69893	-11.93596	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(_{H_2MO})$ (eV)	-31.63534	-63.27074	-31.63541	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom,msp^3.AO)$ (eV)	-1.44915	-2.69893	-1.65376	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(_{MO})$ (eV)	-33.08452	-65.96966	-33.28912	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω $(10^{15}\ rad/s)$	16.4962	59.4034	24.3637	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	10.85807	39.10034	16.03660	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D$ (eV)	-0.21568	-0.40804	-0.26373	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}$ (eV)	0.14655 [28]	0.21077 [12]	0.13638 [35]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}$ (eV)	-0.14240	-0.30266	-0.19554	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mag} (eV)	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(_{Group})$ (eV)	-33.22692	-66.57498	-33.48466	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(_{c_4\ AO/HO})$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(_{c_5\ AO/HO})$ (eV)	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(_{Group})$ (eV)	3.95714	7.80660	4.21488	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.139. The total bond energies of alkyl carboxylic acid anhydrides calculated using the functional group composition and the energies of Table 15.138 compared to the experimental values [3].

Formula	Name	$C-C(O)$ Group	$C=O$ Group	$C-O$ Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_4H_6O_3$	Acetic anhydride	2	2	2	2	0	0	0	0	0	0	0	0	56.94096	56.948	0.00013
$C_6H_{10}O_3$	Propanoic anhydride	2	2	2	2	2	0	2	0	0	0	0	0	81.25636	81.401	0.00177

Table 15.140. The bond angle parameters of alkyl carboxylic acid anhydrides and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle O_aC_aO_b$	2.27954	2.63431	4.3012	-16.17521 O_a	12	-16.47951 O_b	21	0.84115	0.82562	1	1	1	0.83339	-1.44915				122.00	121.7 [36] (acetic anhydride)
$\angle C_aO_bC_a$	2.63431	2.63431	4.4944	-17.30638 C_b	36	-17.30638 C_a	36	0.78617	0.78617	1	1	1	0.78617	-1.85836				117.09	115.8 [36] (acetic anhydride)
$\angle C_bC_aO_b$	2.86175	2.63431	4.4944	-15.55033	5	-13.61806	O	0.87495	0.85395 (Eq. (15.114))	1	1	1	0.86445	-1.44915				109.65	108.3 [36] (acetic anhydride)
$\angle C_bC_aO_a$	2.86175	2.27954	4.6368	-16.47951	21	-13.61806	O	0.82562	0.85395 (Eq. (15.114))	1	1	1	0.83979	-1.65376				128.46	
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	108.6 (acetyl chloride) 108.5 (acetone)
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

NITRILES ($C_nH_{2n-1}N$, $n = 2,3,4,5...\infty$)

The nitriles, $C_nH_{2n-1}N$, comprise a $C \equiv N$ functional group, and the single bond of carbon to the nitrile carbon atom, $C-CN$, is also a functional group. The alkyl portion of the nitrile may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in nitriles are equivalent to those in branched-chain alkanes.

The nitrile $C \equiv N$ is solved equivalently to acetylene as given in the Acetylene Molecule section except that the energy for $\Delta E_{H_2MO}(AO/HO)$ is two times that given in Eq. (14.343), $16.20002\ eV$, in order to match the N AOs to that of the nitrile $C2sp^3$ HO having a bond order of three. $E_T(atom-atom,msp^3.AO)$ of the $C \equiv N$ functional group is $-1.56513\ eV$ (Eq. (14.342)) corresponding to the third-order bonded $C2sp^3$ HO.

The $C-CN$ functional group is equivalent to that of an alkyl $C-C$ group given in the Continuous-Chain Alkanes section except that $E_T(H_2MO)$ and $\overline{E}_{Kvib}$ are those corresponding to a nitrile. As given in the Continuous-Chain Alkanes section, $E_T(atom-atom,msp^3.AO)$ of the alkyl $C-C$ group is $-1.85836\ eV$ where both energy contributions are given by Eq. (14.513). It is based on energy matching within the nitrile. It corresponds to the maximum-magnitude energy contributions of a single-bonded and a third-order bonded $C2sp^3$ HO.

The symbols of the functional groups of nitriles are given in Table 15.141. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of nitriles are given in Tables 15.142, 15.143, and 15.144, respectively. The total energy of each nitrile given in Table 15.139 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.144 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the

$E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of nitriles determined using Eqs. (15.79-15.108) are given in Table 15.146. The C of the $C \equiv N$ group can further bond with only one atom, and the bond is linear as a minimum of energy as in the case of acetylene and alkynes.

Table 15.141. The symbols of functional groups of nitriles.

Functional Group	Group Symbol
C-CN	$C-C$ (i)
CN	$C\equiv N$
CH_3 group	$C-H\left(CH_3\right)$
CH_2 group	$C-H\left(CH_2\right)$
CH (alkyl) group	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.142. The geometrical bond parameters of nitriles and experimental values [1].

Parameter	$C-C$ (i) Group	$C\equiv N$ Group	$C-H\left(CH_3\right)$ Group	$C-H\left(CH_2\right)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\left(a_0\right)$	1.91255	1.20590	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\left(a_0\right)$	1.38295	1.09813	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ $(\AA)$	1.46365	1.16221	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(\AA)$	1.468 (acetonitrile)	1.159 (acetonitrile)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\left(a_0\right)$	1.382110	0.49828	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.72309	0.91064	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.143. The MO to HO intercept geometrical bond parameters of nitriles. R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$RH_2C_bC_a\equiv N$	N	-0.78257	0	0	0		0.93084	0.87170	-15.60832		147.01	32.99	72.28	0.36699	0.73114
$RH_2C_bC_a\equiv N$	C_a	-0.78257	-0.92918	0	0	-153.32744	0.91771	0.82272	-16.53750	-16.34664	145.42	34.58	69.58	0.42077	0.67736
$RH_2C_b-C_aN$	C_a	-0.92918	-0.78257	0	0	-153.32744	0.91771	0.82272	-16.53750	-16.34664	81.32	98.68	38.00	1.50718	0.12423
$H_3C_b-C_aN$	C_b	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	85.50	94.50	40.67	1.45066	0.06771
$RH_2C_cH_2C_b-C_aN$ $R=alkyl$	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	80.53	99.47	37.51	1.51718	0.13423
$C-H\ (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\ (CH)$ (ii)	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.144. The energy parameters (eV) of functional groups of nitriles.

Parameters	$C-C$ (i) Group	$C\equiv N$ Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	3	3	2	1	1	1	1	1	1	1
n_2	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1
c_2	0.91771	0.91140	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	1	0	1	1	0	0	0	1	1	0
c_4	2	6	1	1	1	2	2	2	2	2	2
c_5	0	0	3	2	1	0	0	0	0	0	0
C_{1o}	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	1	1	1	1	1	1	1	1	1	1	1
$V_e\ (eV)$	-33.01231	-207.49229	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_p\ (eV)$	9.83824	37.16984	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
$T\ (eV)$	8.63043	86.03250	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$V_m\ (eV)$	-4.31522	-43.01625	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(_{AO/HO})\ (eV)$	-14.63489	32.40004	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(_{AO/HO})\ (eV)$	-1.85837	0	0	0	0	0	0	0	0	0	0
$E_T(_{AO/HO})\ (eV)$	-12.77652	32.40004	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(_{H_2MO})\ (eV)$	-31.63537	-94.90616	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom,msp^3.AO)\ (eV)$	-1.85836	-1.56513	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(_{MO})\ (eV)$	-33.49374	-96.47124	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\ (10^{15}\ rad/s)$	19.2516	22.0753	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_K\ (eV)$	12.67172	14.53031	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D\ (eV)$	-0.23588	-0.24250	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}\ (eV)$	0.11407 [37]	0.28107 [37]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}\ (eV)$	-0.17884	-0.10197	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{mag}\ (eV)$	0.14803	0.14185	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(_{Group})\ (eV)$	-33.67258	-96.77713	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(_{c_4\ AO/HO})\ (eV)$	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(_{c_5\ AO/HO})\ (eV)$	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(_{Group})\ (eV)$	4.40280	8.82594	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.145. The total bond energies of nitriles calculated using the functional group composition and the energies of Table 15.144 compared to the experimental values [3]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(_{Group})$ (eV) values based on composition is given by (15.58).

Formula	Name	$C-C$ (i) Group	$C\equiv N$ Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_3N	Acetonitrile	1	1	1	0	0	0	0	0	0	0	0	0	25.72060	25.77	0.00174
C_3H_5N	Propanenitrile	1	1	1	1	0	1	0	0	0	0	0	0	37.87830	37.94	0.00171
C_4H_7N	Butanenitrile	1	1	1	2	0	2	0	0	0	0	0	0	50.03600	50.08	0.00082
C_4H_7N	2-Methylpropanenitrile	1	1	2	0	1	0	2	0	0	0	0	0	50.13689	50.18	0.00092
C_5H_9N	Pentanenitrile	1	1	1	3	0	3	0	0	0	0	0	0	62.19370	62.26	0.00111
C_5H_9N	2,2-Dimethylpropanenitrile	1	1	3	0	0	0	0	3	0	0	0	-1	62.47823	62.40	-0.00132
$C_7H_{13}N$	Heptanenitrile	1	1	1	5	0	5	0	0	0	0	0	0	86.50910	86.59	0.00089
$C_8H_{15}N$	Octanenitrile	1	1	1	6	0	6	0	0	0	0	0	0	98.66680	98.73	0.00069
$C_{10}H_{19}N$	Decanenitrile	1	1	1	8	0	8	0	0	0	0	0	0	122.98220	123.05	0.00057
$C_{14}H_{27}N$	Tetradecanenitrile	1	1	1	12	0	12	0	0	0	0	0	0	171.61300	171.70	0.00052

Table 15.146. The bond angle parameters of nitriles and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle C_bC_aN$																		180	
$\angle HC_bH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle HC_bC_a$															70.56			109.44	109.7 (acetonitrile)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	108.5 (acetone)
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

THIOLS ($C_nH_{2n+2}S_m$, $n = 1,2,3,4,5...\infty$)

The alkyl thiols, $C_nH_{2n+2}S_m$, comprise a SH functional group and a $C-S$ functional group. The alkyl portion of the alkyl thiol may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in thiols are equivalent to those in branched-chain alkanes.

The parameters of the SH functional group is solved using Eq. (15.41). As in the case of the $C-H$ bonds of CH_n $n = 1,2,3$, the $S-H$-bond MO is a partial prolate spheroid in between the sulfur and hydrogen nuclei and is continuous with the $S3p$ shell. The energy of the H_2-type ellipsoidal MO is matched to that of the $S3p$ shell and comprises 75% of a H_2-type ellipsoidal MO in order to match potential, kinetic, and orbital energy relationships. Since the energy of S, $E(S) = -10.36001\ eV$, is less that that of H, the linear combination of the H_2-type ellipsoidal MO with the $S3p$ shell further comprises an excess 50% charge-density donation from H to the $S3p$ shell of the $S-H$-bond MO to achieve an energy minimum. The initial total energy of the shell is given by the sum over the four $3p$ electrons. From Eq. (15.12), the sum $E_T(S,3p)$ of the energies of S, S^+, S^{2+}, and S^{3+} [38] is

$$\begin{aligned} E_T(S,3p) &= 10.36001\ eV + 23.33788\ eV + 34.79\ eV + 47.222\ eV \\ &= 115.70989\ eV \end{aligned} \tag{15.118}$$

By considering that the central field decreases by an integer for each successive electron of the shell, the radius r_{3p} of the $S3p$ shell may be calculated from the Coulombic energy using Eqs. (15.13) and (15.118):

$$r_{3p} = \sum_{q=12}^{15} \frac{(Z-q)e^2}{8\pi\varepsilon_0 (e115.70989\ eV)} = \frac{10e^2}{8\pi\varepsilon_0 (e115.70989\ eV)} = 1.17585a_0 \tag{15.119}$$

where $Z = 16$ for sulfur. Using Eqs. (15.14) and (15.119), the Coulombic energy $E_{Coulomb}(S,3p)$ of the outer electron of the $S3p$ shell is

$$E_{Coulomb}(S,3p)=\frac{-e^2}{8\pi\varepsilon_0 r_{3p}}=\frac{-e^2}{8\pi\varepsilon_0 1.17585a_0}=-11.57099\ eV \tag{15.120}$$

The sharing of the electrons between the S and H atoms permits the formation an $S-H$-bond MO that is lowered more in energy than the participating $S3p$ orbital which consequently increases in energy. By considering the 50% electron redistribution in the $S-H$ group as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius r_{S-H3p} of the $S3p$ shell may be calculated from the Coulombic energy using Eq. (15.18)

$$\begin{aligned} r_{S-H3p} &= \left(\sum_{n=12}^{15}(Z-n)+0.25\right)\frac{e^2}{8\pi\varepsilon_0(e115.70989\ eV)} \\ &= \frac{10.5e^2}{8\pi\varepsilon_0(e115.70989\ eV)} \\ &= 1.23465a_0 \end{aligned} \tag{15.121}$$

where the $s=-1$ in Eq. (15.18) due to the charge donation from H to S. Using Eqs. (15.19) and (15.121), the Coulombic energy $E_{Coulomb}(S_{S-H},3p)$ of the outer electron of the $S3p$ shell is

$$\begin{aligned} E_{Coulomb}(S_{S-H},3p) &= \frac{-e^2}{8\pi\varepsilon_0 r_{S-H3p}} \\ &= \frac{-e^2}{8\pi\varepsilon_0 1.23465a_0} \\ &= -11.01999\ eV \end{aligned} \tag{15.122}$$

Thus, $E_T(S-H,3p)$, the energy change of each $S3p$ shell with the formation of the $S-H$-bond MO is given by the difference between Eq. (15.120) and Eq. (15.122):

$$\begin{aligned} E_T(S-H,3p) &= E(S_{S-H},3p)-E(S,3p) \\ &= -11.01999\ eV-(-11.57099\ eV) \\ &= 0.55100\ eV \end{aligned} \tag{15.123}$$

Then, in Eq. (15.42):

$$\begin{aligned} E_T(AO/HO) &= E(S)-E_T(S-H,3p) \\ &= -10.36001\ eV-0.55100\ eV \\ &= -10.91101\ eV \end{aligned} \tag{15.124}$$

And, in Eq. (15.56),

$$E_T(atom-atom,msp^3.AO)=0.55100\ eV \tag{15.125}$$

Due to the charge donation from H to S, $c_1 = 1$ in both Eqs. (15.42) and (15.56). As in the case of the $C-H$-bond MO, $C_1 = 0.75$ based on the orbital composition. In alkyl thiols, the energy of sulfur is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_2 in Eq. (15.52) is also one, and the energy matching condition is determined by the C_2 parameter. Using the energy of S, $E(S) = -10.36001\ eV$ in Eq. (15.65), the hybridization factor C_2 of Eq. (15.52) for the $S-H$-bond MO is

$$C_2(S3p\ to\ H) = \frac{E(S,3p)}{E(H)} = \frac{-10.36001\ eV}{-13.60580\ eV} = 0.76144 \tag{15.126}$$

Since the energy of S is matched to the Coulombic energy between the electron and proton of H, $E(H(a_0))$, $E_{initial}(c_4\ AO/HO) = E(H(a_0)) = -13.60580\ eV$, $E_{initial}(c_5\ AO/HO) = E(H) = -13.59844\ eV$, and E_{mag} is that corresponding to $E(H(a_0))$ given by Eq. (15.58). $E_D(Group)$ for hydrogen sulfide is equivalent to that of the SH functional group, and the $E_D(Group)\ (eV)$ for dihydrogen sulfide follows the same derivation as that for the SH functional group except that the parameters correspond to $n_1 = 2$ rather than $n_1 = 1$ in Eqs. (15.42) and (15.56).

Furthermore, with the energy of S matched to the Coulombic energy between the electron and proton of H, the energy of the $C-S$-bond MO is the sum of the component energies of the H_2-type ellipsoidal MO given in Eq. (15.42) with $E(AO/HO) = 0$ and $E_T(AO/HO) = \Delta E_{H_2MO}(AO/HO)$. Then, the solution of the $C-S$ functional group comprises the hybridization of the $2s$ and $2p$ AOs of C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the S AO to form a MO permits each participating orbital to decrease in radius and energy. Since the energy of sulfur is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243), c_2 in Eq. (15.52) is one, and the energy matching condition is determined by the C_2 parameter. Then, $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3) = -14.63489\ eV$ (Eq. (15.25)), and the S AO has an energy of $E(S) = -10.36001\ eV$. To meet the equipotential condition of the union of the

$C-S$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor C_2 of Eq. (15.51) for the $C-S$-bond MO given by Eqs. (15.68) and (15.70) is

$$C_2\left(C2sp^3HO \ to \ S\right)=\frac{E(S)}{E\left(C,2sp^3\right)}c_2\left(C2sp^3HO\right)=\frac{-10.36001\ eV}{-14.63489\ eV}(0.91771)=0.64965 \quad (15.127)$$

Since the sulfur is energy matched to $E\left(H\left(a_0\right)\right)$ in the $S-H$-bond MO, $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-S$-bond MO in Eq. (15.52) due to the charge donation from the C and S atoms to the MO is $-0.72457\ eV$ corresponding to the energy contribution equivalent to that of a methyl group (Eq. (14.151)).

The symbols of the functional groups of branched-chain alkyl thiols are given in Table 15.147. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl thiols are given in Tables 15.148, 15.149, and 15.150, respectively. The total energy of each alkyl thiol given in Table 15.151 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.150 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)\ (eV)$ values based on composition is given by Eq. (15.58). The $C-C$ bonds to the $HCSH$ group (one H bond to C) were each treated as an iso $C-C$ bond. The $C-C$ bonds to the CSH group (no H bonds to C) were each treated as a tert-butyl $C-C$. E_{mag} was subtracted for each t-butyl group. The bond angle parameters of alkyl thiols determined using Eqs. (15.79-15.108) are given in Table 15.152.

Table 15.147. The symbols of functional groups of alkyl thiols.

Functional Group	Group Symbol
SH group	SH
H_2S	H_2S
C-S	$C-S$
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.148. The geometrical bond parameters of alkyl thiols and experimental values [1].

Parameter	$S-H\ (H_2S)$	SH Group	$C-S$ Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.83762	1.83762	1.90975	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.26842	1.26842	1.71455	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (Å)$	1.34244	1.34244	1.81460	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(Å)$	1.3356	1.34066 (hydrogen sulfide) 1.34 (methanethiol)	1.819 (methanethiol) 1.829 (ethanethiol)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	1.32964	1.32964	0.84112	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.69025	0.69025	0.89778	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.149. The MO to HO intercept geometrical bond parameters of alkyl thiols. R, R', R'' are H or alkyl groups. E_T is $E_T(atom-atom, msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$S-H$ (hydrogen sulfide) (dihydrogen sulfide)	S	0.55100	0	0	0		1.32010	1.23465	-11.01999		108.65	71.35	61.62	0.87355	0.39487
$RS-H$	S	-0.36229	0.55100	0	0		1.32010	0.92955	-14.63704		87.09	92.91	44.28	1.31557	0.04714
C_aH_3-SH	S	-0.36229	0.55100	0	0		1.32010	0.92955	-14.63704		132.06	47.94	55.13	1.09181	0.62274
C_aH_3-SH	C_a	-0.36229	0	0	0	-151.97798	0.91771	0.89582	-15.18804	-14.99717	69.84	110.16	88.87	0.03762	1.67692
$RC'_cH_2C'_bH_2-C'_aH_2SH$	C'_a	-0.36229	-0.92918	0	0	-152.90716	0.91771	0.84418	-16.11722	-15.92636	128.69	51.31	51.57	1.18689	0.52765
$C'-H\ (CH_3)$	C'	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C'-H\ (CH_2)$	C'	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C'-H\ (CH)$	C'	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C'_aC'_bH_2CH_2-$ $(C'-C'\ (a))$	C'_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C'_aC'_bH_2CH_2-$ $(C'-C'\ (a))$	C'_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C'_aC'_b(H_2C'_c-R')HCH_2-$ $(C'-C'\ (b))$	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C'_a(R'-H_2C'_d)C'_b(R''-H_2C'_c)CH_2-$ $(C'-C'\ (c))$	C'_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC'_aC'_b(H_2C'_c-R')HCH_2-$ $(C'-C'\ (d))$	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC'_a(R'-H_2C'_d)C'_b(R''-H_2C'_c)CH_2-$ $(C'-C'\ (e))$	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC'_aC'_b(H_2C'_c-R')HCH_2-$ $(C'-C'\ (f))$	C'_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC'_a(R'-H_2C'_d)C'_b(R''-H_2C'_c)CH_2-$ $(C'-C'\ (f))$	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.150. The energy parameters (eV) of functional groups of alkyl thiols.

Parameters	H_2S	SH Group	$C-S$ Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	2	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.75	0.75	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	0.76144	0.76144	0.64965	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1	1
c_2	1	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	2	1	0	0	1	1	0	0	0	1	1	0
c_4	1	1	2	1	1	1	2	2	2	2	2	2
c_5	1	1	0	3	2	1	0	0	0	0	0	0
C_{1o}	0.75	0.75	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	0.76144	0.76144	0.64965	1	1	1	1	1	1	1	1	1
V_e (eV)	-72.80662	-36.40331	-46.36495	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	21.45310	10.72655	7.93551	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	19.81003	9.90502	12.13899	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_m (eV)	-9.90502	-4.95251	-6.06949	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(AO/HO)$ (eV)	-20.72002	-10.36001	0	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(AO/HO)$ (eV)	1.10200	0.55100	-0.72457	0	0	0	0	0	0	0	0	0
$E_T(AO/HO)$ (eV)	-19.61802	-10.91101	0.72457	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(H_2MO)$ (eV)	-63.27052	-31.63526	-31.63537	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom, msp^3.AO)$ (eV)	1.10200	0.55100	-0.72457	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(MO)$ (eV)	-62.16874	-31.08437	-32.35994	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω $(10^{15}\ rad/s)$	12.5415	12.5415	30.5436	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	8.25504	8.25504	20.10434	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D$ (eV)	-0.17669	-0.17669	-0.28705	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}$ (eV)	0.32422 [39]	0.33620 [40]	0.08146 [41]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}$ (eV)	-0.01458	-0.00859	-0.24632	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mag} (eV)	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(Group)$ (eV)	-31.10493[a]	-31.09296	-32.60626	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(c_4\ AO/HO)$ (eV)	-13.60580	-13.60580	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(c_5\ AO/HO)$ (eV)	-13.59844	-13.59844	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(Group)$ (eV)	3.78628	3.77430	3.33648	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

[a] $E_T(H\text{-}S,H_2S) = E_T(H_2S) - E_T(HS) = 62.19789\ eV - (-31.09296\ eV)$.

Table 15.151. The total bond energies of alkyl thiols calculated using the functional group composition and the energies of Table 15.150 compared to the experimental values [3]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values base composition is given by (15.58).

Formula	Name	H_2S Group	SH Group	$C-S$ Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
HS	Hydrogen Sulfide	1	1	0	0	0	0	0	0	0	0	0	0	0	3.77430	3.653	-0.03320
H_2S	Dihydrogen Sulfide	0	1	0	0	0	0	0	0	0	0	0	0	0	7.56058	7.605	0.00582
CH_4S	Methanethiol	0	1	1	1	0	0	0	0	0	0	0	0	0	19.60264	19.575	-0.00141
C_2H_6S	Ethanethiol	0	1	1	1	1	0	1	0	0	0	0	0	0	31.76034	31.762	0.00005
C_3H_8S	1-Propanethiol	0	1	1	1	2	0	2	0	0	0	0	0	0	43.91804	43.933	0.00035
C_3H_8S	2-Propanethiol	0	1	1	2	0	1	0	2	0	0	0	0	0	44.01893	44.020	0.00003
$C_4H_{10}S$	1-Butanethiol	0	1	1	1	3	0	3	0	0	0	0	0	0	56.07574	56.089	0.00024
$C_4H_{10}S$	2-Butanethiol	0	1	1	2	1	1	1	2	0	0	0	0	0	56.17663	56.181	0.00009
$C_4H_{10}S$	2-Methyl-1-propanethiol	0	1	1	2	1	1	0	3	0	0	0	0	0	56.14830	56.186	0.00066
$C_4H_{10}S$	2-Methyl-2-propanethiol	0	1	1	3	0	0	0	0	3	0	0	0	-1	56.36027	56.313	-0.00084
$C_5H_{12}S$	2-Methyl-1-butanethiol	0	1	1	2	2	1	1	3	0	0	0	0	0	68.30600	68.314	0.00012
$C_5H_{12}S$	1-Pentanethiol	0	1	1	1	4	0	4	0	0	0	0	0	0	68.23344	68.264	0.00044
$C_5H_{12}S$	2-Methyl-2-butanethiol	0	1	1	3	1	0	1	0	3	0	0	0	-1	68.51797	68.441	-0.00113
$C_5H_{12}S$	3-Methyl-2-butanethiol	0	1	1	3	0	2	0	3	0	1	0	0	0	68.31552	68.381	0.00095
$C_5H_{12}S$	2,2-Dimethyl-1-propanethiol	0	1	1	3	1	0	1	0	3	0	0	0	-1	68.51797	68.461	-0.00084
$C_6H_{14}S$	1-Hexanethiol	0	1	1	1	5	0	5	0	0	0	0	0	0	80.39114	80.416	0.00031
$C_6H_{14}S$	2-Methyl-2-pentanethiol	0	1	1	3	2	0	2	0	3	0	0	0	-1	80.67567	80.607	-0.00085
$C_6H_{14}S$	2,3-Dimethyl-2-butanethiol	0	1	1	4	0	1	0	2	2	0	0	1	-1	80.71992	80.603	-0.00145
$C_7H_{16}S$	1-Heptanethiol	0	1	1	1	6	0	6	0	0	0	0	0	0	92.54884	92.570	0.00023
$C_{10}H_{22}S$	1-Decanethiol	0	1	1	1	9	0	9	0	0	0	0	0	0	129.02194	129.048	0.00020

Table 15.152. The bond angle parameters of alkyl thiols and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T\left(atom-atom, msp^3.AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HSC_a$	2.53685	3.42910	4.5166	-10.36001 S	7	-15.75493 C_a	S	0.76144 (Eq. 15.125))	0.86359	0.75	1	0.75	1.13415	0				97.28	96.5 (methanethiol) 96.4 (ethanethiol)
$\angle C_bC_aS$	2.91547	3.42910	5.2344	-16.68412 C_b	25	-10.36001 S	S	0.81549	0.64965 (Eq. (15.127))	1	0.64965 (Eq. (15.127))	1	0.73257	-0.72457				110.92	108.3 (ethanethiol)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

SULFIDES ($C_nH_{2n+2}S_m$, $n = 2,3,4,5...\infty$)

The alkyl sulfides, $C_nH_{2n+2}S_m$, comprise two types of $C-S$ functional groups, one for t-butyl groups corresponding to the C and the other for the remaining general alkyl groups including methyl. The alkyl portion of the alkyl sulfide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in sulfides are equivalent to those in branched-chain alkanes.

Each $C-S$ group is solved by hybridizing the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the S AO to form a MO permits each participating orbital to decrease in radius and energy. Since the energy of sulfur is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243), c_2 in Eq. (15.52) is one, and the energy matching condition is determined by the C_2 parameter. As in the case of thiols, C_2 of Eq. (15.52) for the $C-S$-bond MO given by Eq. (15.127) is $C_2(C2sp^3HO\ to\ S) = 0.64965$.

The $C-S$ group of alkyl sulfides is equivalent to that of thiols where $E_T(atom-atom, msp^3.AO)$ is $-0.72457\ eV$ (Eq. (14.151)). The t-butyl-$C-S$ group is also equivalent to that of thiols except that the energy parameters corresponding to the oscillation in the transition state are matched to those of the t-butyl group.

The symbols of the functional groups of branched-chain alkyl sulfides are given in Table 15.153. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfides are given in Tables 15.154, 15.155, and 15.156, respectively. Consider that the $C-S$ bond is along the x axis in the xy-plane. The S nucleus is at the focus +c and the C nucleus is at the focus –c. The elliptic angle θ' is taken as counterclockwise from the x-axis for S and as clockwise from the –x-axis for C. The total energy of each alkyl sulfide given in Table 15.157 was calculated as the sum

over the integer multiple of each $E_D(Group)$ of Table 15.156 corresponding to functional-group composition of the molecule. E_{mag} given by Eq. (15.58) was subtracted for each t-butyl group. The bond angle parameters of alkyl sulfides determined using Eqs. (15.79-15.108) are given in Table 15.158.

Table 15.153. The symbols of functional groups of alkyl sulfides.

Functional Group	Group Symbol
C-S (methyl, alkyl)	$C-S$ (i)
C-S ($(CH_3)_3C-S-$)	$C-S$ (ii)
CH_3 group	$C-H$ (CH_3)
CH_2 group	$C-H$ (CH_2)
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.154. The geometrical bond parameters of alkyl sulfides and experimental values [1].

Parameter	$C-S$ (i) Group	$C-S$ (ii) Group	$C-H$ (CH_3) Group	$C-H$ (CH_2) Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
a (a_0)	1.90975	1.90975	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
c' (a_0)	1.71455	1.71455	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ $(Å)$	1.81460	1.81460	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(Å)$	1.807 (dimethyl sulfide) 1.813 (ethyl methyl sulfide, avg.)	1.807 (dimethyl sulfide) 1.813 (ethyl methyl sulfide, avg.)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
b,c (a_0)	0.84112	0.84112	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.89778	0.89778	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.155. The MO to HO intercept geometrical bond parameters of alkyl sulfides. R, R', R'' are H or alkyl groups. E_T is $E_T(atom-atom, msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' $(°)$	θ_1 $(°)$	θ_2 $(°)$	d_1 (a_0)	d_2 (a_0)
$R-S-R$ ($C-S$ (i) and (ii))	S	-0.36229	-0.36229	0	0		1.32010	0.87495	-15.55033		129.96	50.04	52.88	1.15262	0.56193
$H_3C_a-S-C_bH_2CH_2R$ ($C-S$ (i))	C_a	-0.36229	0	0	0	-151.97798	0.91771	0.89582	-15.18804	-14.99717	130.79	49.21	53.75	1.12957	0.58518
$H_3C_a-S-C_bH_2CH_2R$ ($C-S$ (i))	C_b	-0.36229	-0.92918	0	0	-152.90716	0.91771	0.84418	-16.11722	-15.92636	128.69	51.31	51.57	1.18689	0.52765
$H_3C_a-S-C_s(CH_3)_3$ ($C-S$ (i) and (ii))	C_s	-0.36229	-0.72457	-0.72457	-0.72457	-154.15170	0.91771	0.78367	-17.36176	-17.17090	125.97	54.03	48.94	1.25430	0.46025
$C-H$ (CH_3)	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H$ (CH_2)	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H$ (CH)	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ ($C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ ($C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.156. The energy parameters (eV) of functional groups of alkyl sulfides.

Parameters	$C-S$ (i) Group	$C-S$ (ii) Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	0.64965	0.64965	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1
c_2	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	0	1	1	0	0	0	1	1	0
c_4	2	2	1	1	1	2	2	2	2	2	2
c_5	0	0	3	2	1	0	0	0	0	0	0
C_{1o}	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	0.64965	0.64965	1	1	1	1	1	1	1	1	1
$V_e\ (eV)$	-46.36495	-46.36495	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_p\ (eV)$	7.93551	7.93551	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
$T\ (eV)$	12.13899	12.13899	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$V_m\ (eV)$	-6.06949	-6.06949	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(AO/HO)\ (eV)$	0	0	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(AO/HO)\ (eV)$	-0.72457	-0.72457	0	0	0	0	0	0	0	0	0
$E_T(AO/HO)\ (eV)$	0.72457	0.72457	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(H_2MO)\ (eV)$	-31.63537	-31.63537	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom,msp^3.AO)\ (eV)$	-0.72457	-0.72457	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(MO)\ (eV)$	-32.35994	-32.35994	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\ (10^{15}\ rad/s)$	30.5436	8.92777	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_K\ (eV)$	20.10434	5.87641	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D\ (eV)$	-0.28705	-0.15519	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}\ (eV)$	0.08146 [41]	0.08146 [41]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}\ (eV)$	-0.24632	-0.11446	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{mag}\ (eV)$	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(Group)\ (eV)$	-32.60626	-32.47440	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(c_4\ AO/HO)\ (eV)$	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(c_5\ AO/HO)\ (eV)$	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(Group)\ (eV)$	3.33648	3.20462	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.157. The total bond energies of alkyl sulfides calculated using the functional group composition and the energies of Table 15.156 compared to the experimental values [3]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_{D(Group)}$ (eV) values based on composition is given by (15.58).

Formula	Name	$C-S$ (i) Group	$C-S$ (ii) Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_6S	Dimethyl sulfide	2	0	2	0	0	0	0	0	0	0	0	0	31.65668	31.672	0.00048
C_3H_8S	Ethyl methyl sulfide	1	0	2	1	0	1	0	0	0	0	0	0	43.81438	43.848	0.00078
$C_4H_{10}S$	Diethyl sulfide	2	0	2	2	0	1	0	0	0	0	0	0	55.97208	56.043	0.00126
$C_4H_{10}S$	Methyl propyl sulfide	2	0	2	2	0	2	0	0	0	0	0	0	55.97208	56.029	0.00102
$C_4H_{10}S$	Isopropyl methyl sulfide	2	0	3	0	1	0	2	0	0	0	0	0	56.07297	56.115	0.00075
$C_5H_{12}S$	Butyl methyl sulfide	2	0	2	3	0	3	0	0	0	0	0	0	68.12978	68.185	0.00081
$C_5H_{12}S$	t-Butyl methyl sulfide	1	1	4	0	0	0	0	3	0	0	0	-1	68.28245	68.381	0.00144
$C_5H_{12}S$	Ethyl propyl sulfide	1	0	2	3	0	3	0	0	0	0	0	0	68.12978	68.210	0.00117
$C_5H_{12}S$	Ethyl isopropyl sulfide	2	0	3	2	1	1	2	0	0	0	0	0	68.23067	68.350	0.00174
$C_6H_{14}S$	Diisopropyl sulfide	2	0	4	0	2	0	4	0	0	0	0	0	80.48926	80.542	0.00065
$C_6H_{14}S$	Butyl ethyl sulfide	2	0	2	4	0	4	0	0	0	0	0	0	80.28748	80.395	0.00133
$C_6H_{14}S$	Methyl pentyl sulfide	2	0	2	4	0	4	0	0	0	0	0	0	80.28748	80.332	0.00056
$C_8H_{18}S$	Dibutyl sulfide	2	0	2	6	0	6	0	0	0	0	0	0	104.60288	104.701	0.00094
$C_8H_{18}S$	Di-sec-butyl sulfide	2	0	4	2	2	2	4	0	0	0	0	0	104.80466	104.701	-0.00099
$C_8H_{18}S$	Di-t-butyl sulfide	0	2	6	0	0	0	0	6	0	0	0	-2	104.90822	104.920	0.00011
$C_8H_{18}S$	Diisobutyl sulfide	2	0	4	2	2	0	6	0	0	0	0	0	104.74800	104.834	0.00082
$C_{10}H_{22}S$	Dipentyl sulfide	2	0	2	8	0	8	0	0	0	0	0	0	128.91828	128.979	0.00047
$C_{10}H_{22}S$	Diisopentyl sulfide	2	0	4	4	2	2	6	0	0	0	0	0	129.06340	129.151	0.00068

Table 15.158. The bond angle parameters of alkyl sulfides and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom, msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle C_aSC_a$ $(C-S\ (i))$	3.42910	3.42910	5.2173	-16.11722	11	-16.11722	11	0.84418	0.84418	1	1	1	0.84418	-1.85836				99.06	99.05 (dimethyl sulfide)
$\angle C_aSC_b$ $(C-S\ (i))$	3.42910	3.42910	5.1381	-15.75493 methyl C_a	7	-16.68412 methylene C_b	25	0.86359	0.81549	1	1	1	0.83954	-1.85836				97.04	97 (ethyl methyl sulfide)
$\angle SC_aC_b$ $(C-S\ (ii))$	3.42910	2.91547	5.3364	-10.36001	S	-16.27490	15	0.64965 (Eq. (15.127))	0.83600	1	0.64965 (Eq. (15.127))	1	0.74282	-0.72457				114.27	114.0 (ethyl methyl sulfide)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	109.3 (dimethyl sulfide) 110 (ethyl methyl sulfide)
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

DISULFIDES ($C_nH_{2n+2}S_{2m}$, $n = 2,3,4,5...\infty$)

The alkyl disulfides, $C_nH_{2n+2}S_{2m}$, comprise $C-S$ and $S-S$ functional groups. The alkyl portion of the alkyl disulfide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in disulfides are equivalent to those in branched-chain alkanes.

Each $C-S$ group is equivalent to that of general alkyl sulfides given in the corresponding section. As in the case of thiols and sulifides, C_2 of Eq. (15.52) for the $C-S$-bond MO given by Eq. (15.127) is $C_2(C2sp^3HO\ to\ \mathrm{S}) = 0.64965$ and $E_T(atom-atom, msp^3.AO)$ is $-0.72457\ eV$ (Eq. (14.151)).

The $S-S$ group is solved as an H_2-type-ellipsoidal-MO that is energy matched to the energy of sulfur, $E(S) = -10.36001\ eV$, such that $E(AO/HO) = -10.36001\ eV$ in Eq. (15.42) with $E_T(AO/HO) = E(AO/HO)$. The $S-S$-bond MO is further energy matched to the $C2sp^3$ HO of the $C-S$-bond MO. C_2 of Eq. (15.52) for the $S-S$-bond MO given by Eq. (15.127) is also $C_2(C2sp^3HO\ to\ \mathrm{S}) = 0.64965$. In order to match $E_T(atom-atom, msp^3.AO)$ of the $C-S$ group ($-0.72457\ eV$ (Eq. (14.151))), $E_T(atom-atom, msp^3.AO)$ of the $S-S$-bond MO is determined using a linear combination of the AOs corresponding to $-0.72457\ eV$ and $0\ eV$ in Eq. (15.29), Eq. (15.31), and Eqs. (15.19-15.20). The result corresponding to bond order 1/2I in Table 15.2 is $E_T(atom-atom, msp^3.AO) = -0.36229\ eV$.

The symbols of the functional groups of branched-chain alkyl disulfides are given in Table 15.159. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl disulfides are given in Tables 15.160, 15.161, and 15.162, respectively. The total energy of each alkyl disulfide given

in Table 15.163 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.162 corresponding to functional-group composition of the molecule. E_{mag} given by Eq. (15.58) was subtracted for each t-butyl group. The bond angle parameters of alkyl disulfides determined using Eqs. (15.79-15.108) are given in Table 15.164.

Table 15.159. The symbols of functional groups of alkyl disulfides.

Functional Group	Group Symbol
C-S	$C-S$
S-S	$S-S$
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.160. The geometrical bond parameters of alkyl disulfides and experimental values [1].

Parameter	$C-S$ (i) Group	$S-S$ Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.90975	2.37173	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.71455	1.91070	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (\mathring{A})$	1.81460	2.02220	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(\mathring{A})$	1.816 (dimethyl disulfide)	2.029 (dimethyl disulfide)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	0.84112	1.40510	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.89778	0.80562	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.161. The MO to HO intercept geometrical bond parameters of alkyl disulfides. R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom, msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$RS-SR$ $(C-S$ (i) and (ii))	S	-0.36229	-0.18114	0	0		1.32010	0.88527	-15.36918		94.25	85.75	38.93	1.84513	0.06558
$H_3C_a-SS-C_bH_2CH_2R$	C_a	-0.36229	0	0	0	-151.97798	0.91771	0.89582	-15.18804	-14.99717	130.79	49.21	53.75	1.12937	0.58518
$H_3C_a-SS-C_bH_2CH_2R$ $(C-S$ (i))	C_b	-0.36229	-0.92918	0	0	-152.90716	0.91771	0.84418	-16.11722	-15.92636	128.69	51.31	51.57	1.18689	0.52765
	C_c	-0.36229	-0.72457	-0.72457	-0.72457	-154.15170	0.91771	0.78367	-17.36176	-17.17090	125.97	54.03	48.94	1.25430	0.46025
$C-H$ (CH_3)	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H$ (CH_2)	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H$ (CH)	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.162. The energy parameters (eV) of functional groups of alkyl disulfides.

Parameters	$C-S$ (i) Group	$S-S$ Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	0.64965	0.64965	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1
c_2	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	0	1	1	0	0	0	1	1	0
c_4	2	2	1	1	1	2	2	2	2	2	2
c_5	0	0	3	2	1	0	0	0	0	0	0
C_{1o}	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	0.64965	0.64965	1	1	1	1	1	1	1	1	1
V_e (eV)	-46.36495	-31.74215	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	7.93551	7.12083	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	12.13899	6.69177	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_m (eV)	-6.06949	-3.34589	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(_{AO/HO})$ (eV)	0	-10.36001	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(_{AO/HO})$ (eV)	-0.72457	0	0	0	0	0	0	0	0	0	0
$E_T(_{AO/HO})$ (eV)	0.72457	-10.36001	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(_{H_2MO})$ (eV)	-31.63537	-31.63544	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom, msp^3.AO)$ (eV)	-0.72457	-0.36229	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(_{MO})$ (eV)	-32.35994	-31.99766	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω $(10^{15}$ $rad/s)$	30.5436	6.45076	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	20.10434	4.24600	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D$ (eV)	-0.28705	-0.13044	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}$ (eV)	0.08146 [41]	0.06745 []	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}$ (eV)	-0.24632	-0.09672	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mag} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(_{Group})$ (eV)	-32.60626	-32.09437	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(_{c_4\ AO/HO})$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(_{c_5\ AO/HO})$ (eV)	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(_{Group})$ (eV)	3.33648	2.82459	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.163. The total bond energies of alkyl disulfides calculated using the functional group composition and the energies of Table 15.162 compared to the experimental values [3]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(_{Group})$ (eV) values based on composition is given by (15.58).

Formula	Name	$C-S$ Group	$S-S$ Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_2H_6S_2$	Dimethyl disulfide	2	1	2	0	0	0	0	0	0	0	0	0	34.48127	34.413	-0.00199
$C_4H_{10}S_2$	Diethyl disulfide	2	1	2	2	0	2	0	0	0	0	0	0	58.79667	58.873	0.00129
$C_6H_{14}S_2$	Dipropyl disulfide	2	1	2	0	4	4	0	0	0	0	0	0	83.11207	83.169	0.00068
$C_8H_{18}S_2$	Di-t-butyl disulfide	2	1	6	0	0	0	0	6	0	0	0	-2	107.99653	107.919	-0.00072

Table 15.164. The bond angle parameters of alkyl disulfides and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom, msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle SC_aH$															70.56			109.44	111.3 (dimethyl disulfide)
$\angle HC_aS$	2.09711	3.42910	4.6220	-15.55033 C_a	5	-10.36001 S	5	0.87495	0.76144 (Eq. (15.126))	0.75	0.76144 (Eq. 15.126))	0.75	0.87026	0				111.22	111.3 (dimethyl disulfide)
$\angle SSC_a$	3.82141	3.42910	5.7017	-10.36001 S	5	-14.82575 C_a	1	0.64965 (Eq. (15.127))	0.91771	1	0.64965 (Eq. (15.127))	1	0.78368	-0.72457				103.57	103.2 (dimethyl disulfide)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

SULFOXIDES ($C_nH_{2n+2}(SO)_m$, $n=2,3,4,5...\infty$)

The alkyl sulfoxides, $C_nH_{2n+2}(SO)_m$, comprise a $C-SO-C$ moiety that comprises $C-S$ and SO functional groups. The alkyl portion of the alkyl sulfoxide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in sulfoxides are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is $1s^22s^22p^4$, and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state $^3P_2$. The SO functional group comprises a double bond between the two unpaired electrons of O. The sulfur atom is energy matched to the $C2sp^3$ HO. In alkyl sulfoxides, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3)=-14.63489\ eV$ (Eq. (15.25)), and the S AO has an initial energy of $E(S)=-10.36001\ eV$ [38]. To meet the equipotential condition of the union of the $S=O$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the $S=O$-bond MO given by Eqs. (15.68) and (15.70) is

$$\begin{aligned} c_2(O\ to\ S3sp^3\ to\ C2sp^3HO) &= \frac{E(O)}{E(S)}c_2(C2sp^3HO) \\ &= \frac{-13.61806\ eV}{-10.36001\ eV}(0.91771) \\ &= 1.20632 \end{aligned} \tag{15.128}$$

The S atom also forms a single bond with each of the $C2sp^3$ HOs of the two $C-S$ groups. The formation of these bonds is permitted by the hybridization of the four electrons of the $S3p$ shell to give the orbital arrangement:

$$\begin{array}{cccc} & 3\mathrm{sp}^3\ \text{state} & & \\ \underline{\uparrow} & \underline{\uparrow} & \underline{\uparrow} & \underline{\uparrow} \\ 0,0 & 1,-1 & 1,0 & 1,1 \end{array} \tag{15.129}$$

where the quantum numbers (ℓ, m_ℓ) are below each electron. The $3s$ shell remains unchanged. Then, the Coulombic energy $E_{Coulomb}(S,3sp^3)$ of the outer electron of the $S3sp^3$ shell given by Eq. (15.118) with $r_{3sp^3} = 1.17585a_0$ (Eq. (15.119)) is $-11.57099\ eV$. Using Eq. (15.16) with the radius of the sulfur atom $r_{16} = 1.32010a_0$ given by Eq. (10.341), the energy $E(S3sp^3)$ of the outer electron of the $S3sp^3$ shell is given by the sum of $E_{Coulomb}(S3sp^3)$ and $E(magnetic)$:

$$\begin{aligned} E(S3sp^3) &= \frac{-e^2}{8\pi\varepsilon_0 r_{3sp^3}} + \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 r_{16}^3} \\ &= \frac{-e^2}{8\pi\varepsilon_0 1.17585a_0} + \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2(1.32010a_0)^3} \\ &= -11.57099\ eV + 0.04973 \\ &= -11.52126\ eV \end{aligned} \tag{15.130}$$

Then, the hybridization energy $E_{hybridization}(S3sp^3)$ of the $S3sp^3$ HO is

$$\begin{aligned} E_{hybridization}(S3sp^3) &= E(S3sp^3) - E(S) \\ &= -11.52126\ eV - 10.36001\ eV \\ &= -1.16125\ eV \end{aligned} \tag{15.131}$$

The SO group is matched to the $C-S$ group with which it shares the common hybridized S atom. Consequently, $E_{hybridization}(S3sp^3)$ is subtracted from $E_T(Group)$ in the determination of $E_D(Group)$ (Eq. 15.56)). Furthermore, the energy of the $S=O$-bond MO is the sum of the component energies of the H_2-type ellipsoidal MO given in Eq. (15.42) with the energy matched to the final energy of the hybridized S atom such that $E(AO/HO) = E(S3sp^3) = -11.52126\ eV$ and $\Delta E_{H_2MO}(AO/HO) = E_{hybridization}(S3sp^3) = -1.16125\ eV$. Then, $E_T(AO/HO) = E(S) = -10.36001\ eV$. Also, $E_T(atom-atom, msp^3.AO)$ of the $S=O$ bond is zero since there are no bonds with a $C2sp^3$ HO.

The $C-S$ group is solved as an energy minimum by hybridizing the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell and by hybridizing the four $S3p$ electrons to form a $S3sp^3$ shell, and the sharing of electrons between the $C2sp^3$ HO and the $S3sp^3$ HO to form a MO permits each participating orbital to decrease in radius and energy. Using the Coulombic

energy of the $S3sp^3$ shell, $E_{Coulomb}\left(S3sp^3\right)$ given by Eq. (15.120) in Eq. (15.63), the $S3sp^3$-shell hybridization factor, $c_2\left(S3sp^3\right)$, is

$$c_2\left(S3sp^3\right)=\frac{E_{Coulomb}\left(S3sp^3\right)}{E(H)}=\frac{-11.57099\ eV}{-13.60580\ eV}=0.85045 \tag{15.132}$$

As in the case of thiols, sulfides, and disulfides, the energy of sulfur is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_1 and c_2 are equal to one in Eq. (15.52), and the energy matching condition is determined by the C_2 parameter. In alkyl sulfoxides, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E\left(C,2sp^3\right)=-14.63489\ eV$ (Eq. (15.25)) and the $S3sp^3$ HO has an energy of $E\left(S3sp^3\right)=-11.52126\ eV$ (Eq. (15.130)). To meet the equipotential condition of the union of the $C-S$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor C_2 of Eq. (15.52) for the $C-S$-bond MO given by Eqs. (15.68) and (15.70) is

$$C_2\left(C2sp^3HO\ to\ S3sp^3\right)=\frac{E\left(S3sp^3\right)}{E\left(C,2sp^3\right)}c_2\left(S3sp^3\right)=\frac{-11.52126\ eV}{-14.63489\ eV}(0.85045)=0.66951 \tag{15.133}$$

As in the case of thiols, sulfides, and disulfides, with the energy of S matched to the Coulombic energy between the electron and proton of H, the energy of the $C-S$-bond MO is the sum of the component energies of the H_2-type ellipsoidal MO given in Eq. (15.42) with $E(AO/HO)=0$ and $E_T\left(AO/HO\right)=\Delta E_{H_2MO}\left(AO/HO\right)$. For sulfoxides, $\Delta E_{H_2MO}\left(AO/HO\right)=-0.72457\ eV$. Further equivalently, $E_T\left(atom-atom,msp^3.AO\right)=-0.72457\ eV$ (Eq. (14.151)).

The symbols of the functional groups of branched-chain alkyl sulfoxides are given in Table 15.165. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfoxides are given in Tables 15.166, 15.167, and 15.168, respectively. Consider that the $C-S$ bond is along the x axis in the xy-plane. The S nucleus is at the focus +c and the C nucleus is at the focus –c. The elliptic angle θ' is taken as counterclockwise from the x-axis for S and as clockwise from the –x-axis for C. The total energy of each alkyl sulfoxide given in Table 15.169 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.168 corresponding to functional-

group composition of the molecule. The bond angle parameters of alkyl sulfoxides determined using Eqs. (15.79-15.108) are given in Table 15.170.

Table 15.165. The symbols of functional groups of alkyl sulfoxides.

Functional Group	Group Symbol
C-S	$C-S$
SO	SO
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.166. The geometrical bond parameters of alkyl sulfoxides and experimental values [1].

Parameter	$C-S$ Group	SO Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.87325	1.98517	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.67271	1.40896	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ ($\AA$)	1.77031	1.49118	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length ($\AA$)	1.799 (dimethyl sulfoxide)	1.485 (dimethyl sulfoxide)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	0.84328	1.39847	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.89294	0.70974	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.167. The MO to HO intercept geometrical bond parameters of alkyl sulfoxides. R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom, msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$R_2S=O$	S	0	-0.36229	-0.36229	0		1.32010	0.87495	-15.55033		79.78	100.22	38.00	1.56425	0.15529
$R_2S=O$	O	0	0	0	0		1.00000	0.91771	-14.82575		84.06	95.94	40.75	1.50400	0.09504
R_2-SO	S	-0.36229	-0.36229	0	0		1.32010	0.87495	-15.55033		129.35	50.65	53.36	1.11799	0.55472
$H_3C_a-S(O)-C_bH_2CH_2R$	C_a	-0.36229	0	0	0	-151.97798	0.91771	0.89582	-15.18804	-14.99717	130.19	49.81	54.24	1.09461	0.57809
$H_3C_a-S(O)-C_bH_2CH_2R$	C_b	-0.36229	-0.92918	0	0	-152.90716	0.91771	0.84418	-16.11722	-15.92636	128.05	51.95	52.03	1.15245	0.52026
$C-H\ (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\ (CH)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ ($C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ ($C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.168. The energy parameters (eV) of functional groups of alkyl sulfoxides.

Parameters	$C-S$ Group	SO Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	2	3	2	1	1	1	1	1	1	1
n_2	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	0.66951	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1
c_2	1	1.20632	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	0	1	1	0	0	0	1	1	0
c_4	2	4	1	1	1	2	2	2	2	2	2
c_5	0	1	3	2	1	0	0	0	0	0	0
C_{1o}	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	0.66951	1	1	1	1	1	1	1	1	1	1
$V_e\ (eV)$	-46.73032	-82.63003	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_p\ (eV)$	8.13401	19.31325	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
$T\ (eV)$	12.47306	20.81183	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$V_m\ (eV)$	-6.23653	-10.40592	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(_{AO/HO})\ (eV)$	0	-11.52126	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(_{AO/HO})\ (eV)$	-0.72457	-1.16125	0	0	0	0	0	0	0	0	0
$E_T(_{AO/HO})\ (eV)$	0.72457	-10.36001	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(_{H_2MO})\ (eV)$	-31.63521	-63.27088	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T\left(atom-atom,msp^3.AO\right)\ (eV)$	-0.72457	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(_{MO})\ (eV)$	-32.35994	-63.27074	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\ \left(10^{15}\ rad/s\right)$	30.8880	17.6762	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_K\ (eV)$	20.33104	11.63476	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D\ (eV)$	-0.28866	-0.21348	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}\ (eV)$	0.08543 [42]	0.12832 [43]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}\ (eV)$	-0.24595	-0.14932	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{mag}\ (eV)$	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(_{Group})\ (eV)$	-32.60589	-63.56937	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(_{c_4\ AO/HO})\ (eV)$	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(_{c_5\ AO/HO})\ (eV)$	0	-1.16125	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(_{Group})\ (eV)$	3.33611	3.86856	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.169. The total bond energies of alkyl sulfoxides calculated using the functional group composition and the energies of Table 15.168 compared to the experimental values [3].

Formula	Name	$C-S$ Group	SO Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_6SO	Dimethyl sulfoxide	2	1	2	0	0	0	0	0	0	0	0	35.52450	35.435	-0.00253
$C_4H_{10}SO$	Diethyl sulfoxide	2	1	2	2	0	2	0	0	0	0	0	59.83990	59.891	0.00085
$C_6H_{14}SO$	Dipropyl sulfoxide	2	1	2	4	0	4	0	0	0	0	0	84.15530	84.294	0.00165

Table 15.170. The bond angle parameters of alkyl sulfoxides and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom, msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle C_aSC_a$	3.34541	3.34541	4.9800	-16.47951	21	-16.47951	21	0.82562	0.82562	1	1	1	0.82562	-1.85836				96.20	96.6 (dimethyl sulfoxide)
$\angle C_aSO$	3.34541	2.81792	4.9598	-15.18804 C_a	2	-13.61806 O	O	0.89582	0.85395 (Eq. (15.114))	1	1	1	0.87489	-1.65376				106.88	106.7 (dimethyl sulfoxide)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	110.3 (dimethyl sulfoxide)
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

SULFOXIDES ($C_nH_{2n+2}(SO)_m$, $n=2,3,4,5...\infty$)

The alkyl sulfoxides, $C_nH_{2n+2}(SO)_m$, comprise a $C-SO-C$ moiety that comprises $C-S$ and SO functional groups. The alkyl portion of the alkyl sulfoxide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in sulfoxides are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is $1s^2 2s^2 2p^4$, and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state $^3P_2$. The SO functional group comprises a double bond between the two unpaired electrons of O. The sulfur atom is energy matched to the $C2sp^3$ HO. In alkyl sulfoxides, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3)=-14.63489\ eV$ (Eq. (15.25)), and the S AO has an initial energy of $E(S)=-10.36001\ eV$ [38]. To meet the equipotential condition of the union of the $S=O$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the $S=O$-bond MO given by Eqs. (15.68) and (15.70) is

$$\begin{aligned} c_2(O\ to\ S3sp^3\ to\ C2sp^3HO) &= \frac{E(O)}{E(S)}c_2(C2sp^3HO) \\ &= \frac{-13.61806\ eV}{-10.36001\ eV}(0.91771) \\ &= 1.20632 \end{aligned} \tag{15.128}$$

The S atom also forms a single bond with each of the $C2sp^3$ HOs of the two $C-S$ groups. The formation of these bonds is permitted by the hybridization of the four electrons of the $S3p$ shell to give the orbital arrangement:

$$\begin{array}{cccc} \multicolumn{4}{c}{3\text{sp}^3\text{ state}} \\ \underline{\uparrow} & \underline{\uparrow} & \underline{\uparrow} & \underline{\uparrow} \\ 0,0 & 1,-1 & 1,0 & 1,1 \end{array} \tag{15.129}$$

where the quantum numbers (ℓ, m_ℓ) are below each electron. The $3s$ shell remains unchanged. Then, the Coulombic energy $E_{Coulomb}(S,3sp^3)$ of the outer electron of the $S3sp^3$ shell given by Eq. (15.118) with $r_{3sp^3} = 1.17585a_0$ (Eq. (15.119)) is $-11.57099\ eV$. Using Eq. (15.16) with the radius of the sulfur atom $r_{16} = 1.32010a_0$ given by Eq. (10.341), the energy $E(S3sp^3)$ of the outer electron of the $S3sp^3$ shell is given by the sum of $E_{Coulomb}(S3sp^3)$ and $E(magnetic)$:

$$\begin{aligned} E(S3sp^3) &= \frac{-e^2}{8\pi\varepsilon_0 r_{3sp^3}} + \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 r_{16}^3} \\ &= \frac{-e^2}{8\pi\varepsilon_0 1.17585a_0} + \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 (1.32010a_0)^3} \\ &= -11.57099\ eV + 0.04973 \\ &= -11.52126\ eV \end{aligned} \tag{15.130}$$

Then, the hybridization energy $E_{hybridization}(S3sp^3)$ of the $S3sp^3$ HO is

$$\begin{aligned} E_{hybridization}(S3sp^3) &= E(S3sp^3) - E(S) \\ &= -11.52126\ eV - 10.36001\ eV \\ &= -1.16125\ eV \end{aligned} \tag{15.131}$$

The SO group is matched to the $C-S$ group with which it shares the common hybridized S atom. Consequently, $E_{hybridization}(S3sp^3)$ is subtracted from $E_T(Group)$ in the determination of $E_D(Group)$ (Eq. 15.56)). Furthermore, the energy of the $S=O$-bond MO is the sum of the component energies of the H_2-type ellipsoidal MO given in Eq. (15.42) with the energy matched to the final energy of the hybridized S atom such that $E(AO/HO) = E(S3sp^3) = -11.52126\ eV$ and $\Delta E_{H_2MO}(AO/HO) = E_{hybridization}(S3sp^3) = -1.16125\ eV$. Then, $E_T(AO/HO) = E(S) = -10.36001\ eV$. Also, $E_T(atom-atom, msp^3.AO)$ of the $S=O$ bond is zero since there are no bonds with a $C2sp^3$ HO.

The $C-S$ group is solved as an energy minimum by hybridizing the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell and by hybridizing the four $S3p$ electrons to form a $S3sp^3$ shell, and the sharing of electrons between the $C2sp^3$ HO and the $S3sp^3$ HO to form a MO permits each participating orbital to decrease in radius and energy. Using the Coulombic

energy of the $S3sp^3$ shell, $E_{Coulomb}\left(S3sp^3\right)$ given by Eq. (15.120) in Eq. (15.63), the $S3sp^3$-shell hybridization factor, $c_2\left(S3sp^3\right)$, is

$$c_2\left(S3sp^3\right) = \frac{E_{Coulomb}\left(S3sp^3\right)}{E(H)} = \frac{-11.57099\ eV}{-13.60580\ eV} = 0.85045 \tag{15.132}$$

As in the case of thiols, sulfides, and disulfides, the energy of sulfur is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_1 and c_2 are equal to one in Eq. (15.52), and the energy matching condition is determined by the C_2 parameter. In alkyl sulfoxides, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E\left(C,2sp^3\right) = -14.63489\ eV$ (Eq. (15.25)) and the $S3sp^3$ HO has an energy of $E\left(S3sp^3\right) = -11.52126\ eV$ (Eq. (15.130)). To meet the equipotential condition of the union of the $C-S$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor C_2 of Eq. (15.52) for the $C-S$-bond MO given by Eqs. (15.68) and (15.70) is

$$C_2\left(C2sp^3HO\ to\ S3sp^3\right) = \frac{E\left(S3sp^3\right)}{E\left(C,2sp^3\right)} c_2\left(S3sp^3\right) = \frac{-11.52126\ eV}{-14.63489\ eV}(0.85045) = 0.66951 \tag{15.133}$$

As in the case of thiols, sulfides, and disulfides, with the energy of S matched to the Coulombic energy between the electron and proton of H, the energy of the $C-S$-bond MO is the sum of the component energies of the H_2-type ellipsoidal MO given in Eq. (15.42) with $E(AO/HO) = 0$ and $E_T\left(AO/HO\right) = \Delta E_{H_2MO}\left(AO/HO\right)$. For sulfoxides, $\Delta E_{H_2MO}\left(AO/HO\right) = -0.72457\ eV$. Further equivalently, $E_T\left(atom-atom, msp^3.AO\right) = -0.72457\ eV$ (Eq. (14.151)).

The symbols of the functional groups of branched-chain alkyl sulfoxides are given in Table 15.165. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfoxides are given in Tables 15.166, 15.167, and 15.168, respectively. Consider that the $C-S$ bond is along the x axis in the xy-plane. The S nucleus is at the focus +c and the C nucleus is at the focus –c. The elliptic angle θ' is taken as counterclockwise from the x-axis for S and as clockwise from the –x-axis for C. The total energy of each alkyl sulfoxide given in Table 15.169 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.168 corresponding to functional-

group composition of the molecule. The bond angle parameters of alkyl sulfoxides determined using Eqs. (15.79-15.108) are given in Table 15.170.

Table 15.165. The symbols of functional groups of alkyl sulfoxides.

Functional Group	Group Symbol
C-S	$C-S$
SO	SO
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.166. The geometrical bond parameters of alkyl sulfoxides and experimental values [1].

Parameter	$C-S$ Group	SO Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.87325	1.98517	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.67271	1.40896	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (Å)$	1.77031	1.49118	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(Å)$	1.799 (dimethyl sulfoxide)	1.485 (dimethyl sulfoxide)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	0.84328	1.39847	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.89294	0.70974	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.167. The MO to HO intercept geometrical bond parameters of alkyl sulfoxides. R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' $(°)$	θ_1 $(°)$	θ_2 $(°)$	d_1 (a_0)	d_2 (a_0)
$R_2S=O$	S	0	-0.36229	-0.36229	0		1.32010	0.87495	-15.55033		79.78	100.22	38.00	1.56425	0.15529
$R_2S=O$	O	0	0	0	0		1.00000	0.91771	-14.82575		84.06	95.94	40.75	1.50400	0.09504
R_2-SO	S	-0.36229	-0.36229	0	0		1.32010	0.87495	-15.55033		129.35	50.65	53.36	1.11799	0.55472
$H_3C_a-S(O)-C_bH_2CH_2R$	C_a	-0.36229	0	0	0	-151.97798	0.91771	0.89582	-15.18804	-14.99717	130.19	49.81	54.24	1.09461	0.57809
$H_3C_a-S(O)-C_bH_2CH_2R$	C_b	-0.36229	-0.92918	0	0	-152.90716	0.91771	0.84418	-16.11722	-15.92636	128.05	51.95	52.03	1.15245	0.52026
$C-H\ (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\ (CH)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ ($C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ ($C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.168. The energy parameters (eV) of functional groups of alkyl sulfoxides.

Parameters	$C-S$ Group	SO Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	2	3	2	1	1	1	1	1	1	1
n_2	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	0.66951	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1
c_2	1	1.20632	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	0	1	1	0	0	0	1	1	0
c_4	2	4	1	1	1	2	2	2	2	2	2
c_5	0	1	3	2	1	0	0	0	0	0	0
C_{1o}	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	0.66951	1	1	1	1	1	1	1	1	1	1
V_e (eV)	-46.73032	-82.63003	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	8.13401	19.31325	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	12.47306	20.81183	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_m (eV)	-6.23653	-10.40592	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(_{AO/HO})$ (eV)	0	-11.52126	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(_{AO/HO})$ (eV)	-0.72457	-1.16125	0	0	0	0	0	0	0	0	0
$E_T(_{AO/HO})$ (eV)	0.72457	-10.36001	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(_{H_2MO})$ (eV)	-31.63521	-63.27088	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom,msp^3.AO)$ (eV)	-0.72457	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(_{MO})$ (eV)	-32.35994	-63.27074	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω $(10^{15}\ rad/s)$	30.8880	17.6762	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	20.33104	11.63476	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D$ (eV)	-0.28866	-0.21348	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}$ (eV)	0.08543 [42]	0.12832 [43]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}$ (eV)	-0.24595	-0.14932	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mag} (eV)	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(_{Group})$ (eV)	-32.60589	-63.56937	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(c_4\ AO/HO)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(c_5\ AO/HO)$ (eV)	0	-1.16125	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(_{Group})$ (eV)	3.33611	3.86856	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.169. The total bond energies of alkyl sulfoxides calculated using the functional group composition and the energies of Table 15.168 compared to the experimental values [3].

Formula	Name	$C-S$ Group	SO Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_6SO	Dimethyl sulfoxide	2	1	2	0	0	0	0	0	0	0	0	35.52450	35.435	-0.00253
$C_4H_{10}SO$	Diethyl sulfoxide	2	1	2	2	0	2	0	0	0	0	0	59.83990	59.891	0.00085
$C_6H_{14}SO$	Dipropyl sulfoxide	2	1	2	4	0	4	0	0	0	0	0	84.15530	84.294	0.00165

Table 15.170. The bond angle parameters of alkyl sulfoxides and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom, msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle C_aSC_a$	3.34541	3.34541	4.9800	-16.47951	21	-16.47951	21	0.82562	0.82562	1	1	1	0.82562	-1.85836				96.20	96.6 (dimethyl sulfoxide)
$\angle C_aSO$	3.34541	2.81792	4.9598	-15.18804 C_a	2	-13.61806 O	O	0.89582	0.85395 (Eq. (15.114))	1	1	1	0.87489	-1.65376				106.88	106.7 (dimethyl sulfoxide)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	110.3 (dimethyl sulfoxide)
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

DIMETHYL SULFOXIDE DIHEDRAL ANGLE

The dihedral angle $\theta_{\angle S=O/CSC}$ between the plane defined by the CSC MO comprising a linear combination of two $S-C$-bond MOs and a line defined by the $S=O$-bond MO where S is the central atom is calculated using the results given in Table 15.170 and Eqs. (15.105-15.108). The distance d_1 along the bisector of $\theta_{\angle CSC}$ from S to the internuclear-distance line between C and C, $2c'_{C-C}$, is given by

$$d_1 = 2c'_{S-C}\cos\frac{\theta_{\angle CSC}}{2} = 4.9800a_0\cos\frac{96.20^\circ}{2} = 2.23423a_0 \tag{15.134}$$

where $2c'_{S-C}$ is the internuclear distance between S and C. The atoms C, C, and O define the base of a pyramid. Then, the pyramidal angle $\theta_{\angle COC}$ can be solved from the internuclear distances between C and C, $2c'_{C-C}$, and between C and O, $2c'_{C-O}$, using the law of cosines (Eq. (15.106)):

$$\begin{aligned}\theta_{\angle COC} &= \cos^{-1}\left(\frac{(2c'_{C-O})^2+(2c'_{C-O})^2-(2c'_{C-C})^2}{2(2c'_{C-O})(2c'_{C-O})}\right)\\ &= \cos^{-1}\left(\frac{(4.95984)^2+(4.95984)^2-(4.9800)^2}{2(4.95984)(4.95984)}\right)\\ &= 60.27^\circ\end{aligned} \tag{15.135}$$

Then, the distance d_2 along the bisector of $\theta_{\angle COC}$ from O to the internuclear-distance line $2c'_{C-C}$, is given by

$$d_2 = 2c'_{C-O}\cos\frac{\theta_{\angle COC}}{2} = 4.95984a_0\cos\frac{60.27^\circ}{2} = 4.28952a_0 \tag{15.136}$$

The lengths d_1, d_2, and $2c'_{S=O}$ define a triangle wherein the angle between d_1 and the internuclear distance between O and S, $2c'_{S=O}$, is the dihedral angle $\theta_{\angle S=O/CSC}$ that can be solved using the law of cosines (Eq. (15.108)):

$$\begin{aligned}\theta_{\angle S=O/CSC} &= \cos^{-1}\left(\frac{d_1^2+(2c'_{S=O})^2-d_2^2}{2d_1(2c'_{S=O})}\right)\\ &= \cos^{-1}\left(\frac{(2.23423)^2+(2.81792)^2-(4.28952)^2}{2(2.23423)(2.81792)}\right)\\ &= 115.74^\circ\end{aligned} \tag{15.137}$$

The experimental [1] dihedral angle $\theta_{\angle S=O/CSC}$ is

$$\theta_{\angle S=O/CSC} = 115.5° \tag{15.138}$$

SULFITES ($C_nH_{2n+2}(SO_3)_m$, $n = 2,3,4,5...\infty$)

The alkyl sulfites, $C_nH_{2n+2}(SO_3)_m$, comprise a $C-O-SO-O-C$ moiety that comprises two types $C-O$ functional groups, one for methyl and one for alkyl, and $O-S$ and SO functional groups. The alkyl portion of the alkyl sulfite may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in sulfites are equivalent to those in branched-chain alkanes.

The SO functional group is equivalent to that of sulfoxides with $E_T(atom-atom,msp^3.AO)=0$ as given in the Sulfoxides section. The methyl and alkyl $C-O$ functional groups having $E_T(atom-atom,msp^3.AO)=-1.44915\ eV$ and $E_T(atom-atom,msp^3.AO)=-1.65376\ eV$, respectively, are equivalent to the corresponding ether groups given in the Ethers section except for the energy terms corresponding to oscillation of the bond in the transition state.

The electron configuration of oxygen is $1s^22s^22p^4$, and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state $^3P_2$. The SO functional group comprises a double bond between the S atom and the two unpaired electrons of O. The S atom also forms single bonds with two additional oxygen atoms that are each further bound to methyl or alkyl groups. The first bond-order bonding in the $O-S$ groups is between the sulfur atom and a $O2p$ AO of each oxygen of the two bonds. The formation of these four bonds with the sulfur atom is permitted by the hybridization of the four electrons of the $S3p$ shell to give the orbital arrangement given by Eq. (15.129). Then, the Coulombic energy $E_{Coulomb}(S,3sp^3)$ of the outer electron of the $S3sp^3$ shell given by Eq. (15.120) with $r_{3sp^3}=1.17585a_0$ (Eq. (15.119)) is $-11.57099\ eV$. Using Eq. (15.16) with the radius of the

sulfur atom $r_{16} = 1.32010a_0$ given by Eq. (10.341), the energy $E(S3sp^3)$ of the outer electron of the $S3sp^3$ shell given by the sum of $E_{Coulomb}(S3sp^3)$ and $E(magnetic)$ is $E(S3sp^3) = -11.52126\ eV$ (Eq. (15.130)).

Thus, the $O-S$ group is solved as an energy minimum by hybridizing the four $S3p$ electrons to form a $S3sp^3$ shell, and the sharing of electrons between the $O2p$ AO and the $S3sp^3$ HO to form a MO permits each participating orbital to decrease in radius and energy. As in the case of thiols, sulfides, disulfides, and sulfoxides, the energy of sulfur is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_1 and c_2 are equal to one in Eq. (15.52), and the energy matching condition is determined by the C_2 parameter. Each $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3) = -14.63489\ eV$ (Eq. (15.25)), and the S HO has an energy of $E(S3sp^3) = -11.52126\ eV$. To meet the equipotential condition of the union of the $O-S$ H_2-type-ellipsoidal-MO with these orbitals with the oxygen that further bonds to a $C2sp^3$ HO, the hybridization factor C_2 of Eq. (15.52) for the $O-S$-bond MO given by Eqs. (15.68) and (15.70) is

$$\begin{aligned} C_2\left(S3sp^3 \text{ to } O \text{ to } C2sp^3HO\right) &= \frac{E\left(S,3sp^3\right)}{E(O,2p)} c_2\left(C2sp^3HO\right) \\ &= \frac{-11.52126\ eV}{-13.61806\ eV}(0.91771) \\ &= 0.77641 \end{aligned} \tag{15.139}$$

As in the case of thiols, sulfides, disulfides, and sulfoxides, with the energy of S matched to the Coulombic energy between the electron and proton of H, the energy of the $O-S$-bond MO is the sum of the component energies of the H_2-type ellipsoidal MO given in Eq. (15.42) with $E(AO/HO) = 0$ and $E_T(AO/HO) = \Delta E_{H_2MO}(AO/HO)$. For sulfites, $\Delta E_{H_2MO}(AO/HO) = -0.92918\ eV$ and equivalently, $E_T(atom-atom, msp^3.AO) = -0.92918\ eV$ (Eq. (14.513)) due to the maximum energy match with the oxygen AO as in the case with carboxylic acid esters.

The symbols of the functional groups of branched-chain alkyl sulfites are given in Table 15.177. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfites are given in Tables 15.178, 15.179, and 15.180, respectively. The total energy of each alkyl sulfite given in Table 15.175 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.180 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl sulfites determined using Eqs. (15.79-15.108) are given in Table 15.182.

Table 15.177. The symbols of functional groups of alkyl sulfites.

Functional Group	Group Symbol
C-O (methyl)	$C-O$ (i)
C-O (alkyl)	$C-O$ (ii)
O-SO_2	$O-S$
SO	SO
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.178. The geometrical bond parameters of alkyl sulfites and experimental values [1].

Parameter	$C-O$ (i) Group	$C-O$ (ii) Group	$O-S$	SO	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.80717	1.79473	1.70299	1.98517	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.34431	1.33968	1.48102	1.40896	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ (Å)	1.42276	1.41785	1.56744	1.49118	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)			1.574 (H_2SO_4)	1.485 (dimethyl sulfoxide)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b, c\ (a_0)$	1.20776	1.19429	0.84069	1.39847	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.74388	0.74645	0.86966	0.70974	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.179. The MO to HO intercept geometrical bond parameters of alkyl sulfites. R, R', R'' are H or alkyl groups. E_T is $E_T(atom-atom, msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$(RO)_2S=O_u$	S	0	-0.46459	-0.46459	0		1.32010	0.86359	-15.75493		78.56	101.44	37.25	1.58026	0.17130
$(RO)_2S=O_u$	O_a	0	0	0	0		1.00000	0.91771	-14.82575		84.06	95.94	40.75	1.50400	0.09504
$CH_3O_u-S(O)OR'$	S	-0.46459	-0.46459	0	0		1.32010	0.86359	-15.75493		126.68	53.32	55.47	0.96521	0.51581
$CH_3O_u-S(O)OR'$ $(C-O$ (i))	O_a	-0.46459	-0.72457	0	0		1.00000	0.84957	-16.01492		126.03	53.97	54.81	0.98133	0.49969
$RCH_2O_u-S(O)OR'$ $(C-O$ (ii))	O_a	-0.46459	-0.82688	0	0		1.00000	0.84418	-16.11722		125.77	54.23	54.56	0.98753	0.49349
$H_3C_u-O_aS(O)OR$ $(C-O$ (i))	O_a	-0.72457	-0.46459	0	0		1.00000	0.84957	-16.01492		93.85	86.15	44.57	1.28731	0.05700
$H_3C_u-O_aS(O)OR$ $(C-O$ (i))	C_a	-0.72457	0	0	0	-152.34026	0.91771	0.87495	-15.55033	-15.35946	95.98	84.02	46.10	1.25319	0.09112
$RH_2C_u-O_aS(O)OR'$ $(C-O$ (ii))	O_a	-0.82688	-0.46459	0	0		1.00000	0.84418	-16.11722		94.50	85.50	44.80	1.27343	0.06624
$RH_2C_u-O_aS(O)OR'$ $(C-O$ (ii))	C_a	-0.82688	-0.92918	0	0	-153.37175	0.91771	0.82053	-16.58181	-16.39095	92.41	87.59	43.35	1.30512	0.03456
$C-H$ (CH_3)	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H$ (CH_2)	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H$ (CH)	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.180. The energy parameters (eV) of functional groups of alkyl sulfites.

Parameters	$C-O$ (i) Group	$C-O$ (ii) Group	$O-S$ Group	SO Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	1	1	2	3	2	1	1	1	1	1	1	1
n_2	0	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	0.77641	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1	1	1
c_2	0.85395	0.85395	1	1.20632	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	0	0	0	1	1	0	0	0	1	1	0
c_4	2	2	2	4	1	1	1	2	2	2	2	2	2
c_5	0	0	0	1	3	2	1	0	0	0	0	0	0
C_{1o}	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	1	1	0.77641	1	1	1	1	1	1	1	1	1	1
$V_e\ (eV)$	-33.15757	-33.47304	-48.93512	-82.63003	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_p\ (eV)$	10.12103	10.15605	9.18680	19.31325	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
$T\ (eV)$	9.17389	9.32537	14.36741	20.81183	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$V_m\ (eV)$	-4.58695	-4.66268	-7.18371	-10.40592	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(_{AO/HO})\ (eV)$	-14.63489	-14.63489	0	-11.52126	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(_{AO/HO})\ (eV)$	-1.44915	-1.65376	-0.92918	-1.16125	0	0	0	0	0	0	0	0	0
$E_T(_{AO/HO})\ (eV)$	-13.18574	-12.98113	0.92918	-10.36001	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(_{H_2MO})\ (eV)$	-31.63533	-31.63544	-31.63543	-63.27088	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom,msp^3.AO)\ (eV)$	-1.44915	-1.65376	-0.92918	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(_{MO})\ (eV)$	-33.08452	-33.28912	-32.56455	-63.27074	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\ (10^{15}\ rad/s)$	22.0240	12.1583	33.4164	17.6762	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_K\ (eV)$	14.49660	8.00277	21.99527	11.63476	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D\ (eV)$	-0.24921	-0.18631	-0.30214	-0.21348	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}\ (eV)$	0.13663 [21]	0.13663 [21]	0.08679 [42]	0.12832 [43]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}\ (eV)$	-0.18089	-0.11799	-0.25875	-0.14932	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{mag}\ (eV)$	0.14803	0.14803	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(_{Group})\ (eV)$	-33.26541	-33.40711	-32.82330	-63.56937	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(_{c_4\ AO/HO})\ (eV)$	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(_{c_5\ AO/HO})\ (eV)$	0	0	0	-1.16125	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(_{Group})\ (eV)$	3.99563	4.13733	3.55352	3.86856	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.181. The total bond energies of alkyl sulfites calculated using the functional group composition and the energies of Table 15.180 compared to the experimental values [3].

Formula	Name	$C-O$ (i) Group	$C-O$ (ii) Group	$O-S$ Group	SO Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_2H_6SO_3$	Dimethyl sulfite	2	0	2	1	2	0	0	0	0	0	0	0	0	43.95058	44.042	0.00207
$C_4H_{10}SO_3$	Diethyl sulfite	0	2	2	1	2	2	0	2	0	0	0	0	0	68.54939	68.648	0.00143
$C_8H_{18}SO_3$	Dibutyl sulfite	0	2	2	1	2	6	0	6	0	0	0	0	0	117.18019	117.191	0.00009

Table 15.182. The bond angle parameters of alkyl sulfites and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	2c' Bond 1 (a_0)	2c' Bond 2 (a_0)	2c' Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle O_aSO_b$	2.81792	2.96203	4.6904	-15.95954 O_a	9	-16.11722 O_c	11	0.85252	0.84418	1	1	1	0.84835	-1.65376				108.46	
$\angle O_bSO_c$	2.96203	2.96203	4.6476	-16.11722 O_b	11	-16.11722 O_c	11	0.84418	0.84418	1	1	1	0.84418	-1.65376				103.35	
$\angle C_aO_bS$	2.68862	2.96203	4.8416	-15.75493 C_a	7	-10.36001 S	S	0.86359	0.77641 (Eq. (15.139))	1	0.77641 (Eq. (15.139))	1	0.82000	-0.72457				117.84	
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

SULFATES ($C_nH_{2n+2}\left(SO_4\right)_m$, $n = 2,3,4,5...\infty$)

The alkyl sulfates, $C_nH_{2n+2}\left(SO_4\right)_m$, comprise a $C-O-SO_2-O-C$ moiety that comprises two types $C-O$ functional groups, one for methyl and one for alkyl, and $O-S$ and SO_2 functional groups. The alkyl portion of the alkyl sulfate may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in sulfates are equivalent to those in branched-chain alkanes.

The methyl and alkyl $C-O$ functional groups having $E_T\left(atom-atom,msp^3.AO\right) = -1.44915\ eV$ and $E_T\left(atom-atom,msp^3.AO\right) = -1.65376\ eV$, respectively, are equivalent to the corresponding groups given in the Sulfites section. The $O-S$ functional group having $E_T\left(atom-atom,msp^3.AO\right) = -0.92918\ eV$ is equivalent to that given in the Sulfites section. The SO_2 functional group is equivalent to that of sulfones with $E_T\left(atom-atom,msp^3.AO\right) = 0$ as given in the Sulfones section.

The symbols of the functional groups of branched-chain alkyl sulfates are given in Table 15.183. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfates are given in Tables 15.184, 15.185, and 15.186, respectively. The total energy of each alkyl sulfate given in Table 15.187 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.186 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl sulfates determined using Eqs. (15.79-15.108) are given in Table 15.188.

Table 15.183. The symbols of functional groups of alkyl sulfates.

Functional Group	Group Symbol
C-O (methyl)	$C-O$ (i)
C-O (alkyl)	$C-O$ (ii)
O-SO_3	$O-S$
SO_2	SO_2
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.184. The geometrical bond parameters of alkyl sulfates and experimental values [1].

Parameter	$C-O$ (i) Group	$C-O$ (ii) Group	$O-S$	SO_2	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.80717	1.79473	1.70299	1.85851	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.34431	1.33968	1.48102	1.36327	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (Å)$	1.42276	1.41785	1.56744	1.44282	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(Å)$			1.574 (H_2SO_4)	1.435 (dimethyl sulfone)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	1.20776	1.19429	0.84069	1.26315	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.74388	0.74645	0.86966	0.73353	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.185. The MO to HO intercept geometrical bond parameters of alkyl sulfates. R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulombic}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' $(^\circ)$	θ_1 $(^\circ)$	θ_2 $(^\circ)$	d_1 (a_0)	d_2 (a_0)
$(RO)_2(O_a)S=O_a$	S	0	0	-0.46459	-0.46459		1.32010	0.86359	-15.75493		90.46	89.54	43.13	1.35635	0.00693
$(RO)_2(O_a)S=O_a$	O_a	0	0	0	0		1.00000	0.91771	-14.82575		95.05	84.95	46.36	1.28256	0.08071
$CH_3O_a-S(O_2)OR'$	S	-0.46459	-0.46459	0	0		1.32010	0.86359	-15.75493		126.68	53.32	55.47	0.96521	0.51581
$CH_3O_a-S(O_2)OR'$ $(C-O$ (i))	O_a	-0.46459	-0.72457	0	0		1.00000	0.84957	-16.01492		126.03	53.97	54.81	0.98133	0.49969
$RCH_2O_a-S(O_2)OR'$ $(C-O$ (ii))	O_a	-0.46459	-0.82688	0	0		1.00000	0.84418	-16.11722		125.77	54.23	54.56	0.98753	0.49349
$H_3C_a-O_aS(O_2)OR$ $(C-O$ (i))	O_a	-0.72457	-0.46459	0	0		1.00000	0.84957	-16.01492		93.85	86.15	44.57	1.28731	0.05700
$H_3C_a-O_aS(O_2)OR$ $(C-O$ (i))	C_a	-0.72457	0	0	0	-152.34026	0.91771	0.87495	-15.55033	-15.35946	95.98	84.02	46.10	1.25319	0.09112
$RH_2C_a-O_aS(O_2)OR'$ $(C-O$ (ii))	O_a	-0.82688	-0.46459	0	0		1.00000	0.84418	-16.11722		94.50	85.50	44.80	1.27343	0.06624
$RH_2C_a-O_aS(O_2)OR'$ $(C-O$ (ii))	C_a	-0.82688	-0.92918	0	0	-153.37175	0.91771	0.82053	-16.58181	-16.39095	92.41	87.59	43.35	1.30512	0.03456
$C-H\ (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\ (CH)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.186. The energy parameters (eV) of functional groups of alkyl sulfates.

Parameters	$C-O$ (i) Group	$C-O$ (ii) Group	$O-S$ Group	SO_2 Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	1	1	4	3	2	1	1	1	1	1	1	1
n_2	0	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	0.77641	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1	1	1
c_2	0.85395	0.85395	1	1.20632	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	0	1	0	1	1	0	0	0	1	1	0
c_4	2	2	2	8	1	1	1	2	2	2	2	2	2
c_5	0	0	0	1	3	2	1	0	0	0	0	0	0
C_{1o}	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	1	1	0.77641	1	1	1	1	1	1	1	1	1	1
$V_e\ (eV)$	-33.15757	-33.47304	-48.93512	-180.36454	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_p\ (eV)$	10.12103	10.15605	9.18680	39.92103	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
$T\ (eV)$	9.17389	9.32537	14.36741	48.52397	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$V_m\ (eV)$	-4.58695	-4.66268	-7.18371	-24.26198	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(_{AO/HO})\ (eV)$	-14.63489	-14.63489	0	-11.52126	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(_{AO/HO})\ (eV)$	-1.44915	-1.65376	-0.92918	-1.16125	0	0	0	0	0	0	0	0	0
$E_T(_{AO/HO})\ (eV)$	-13.18574	-12.98113	0.92918	-10.36001	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(_{H_2MO})\ (eV)$	-31.63533	-31.63544	-31.63543	-126.54154	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom,msp^3.AO)\ (eV)$	-1.44915	-1.65376	-0.92918	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(_{MO})\ (eV)$	-33.08452	-33.28912	-32.56455	-126.54147	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\ (10^{15}\ rad/s)$	22.0240	12.1583	33.4164	11.5378	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_K\ (eV)$	14.49660	8.00277	21.99527	7.59437	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D\ (eV)$	-0.24921	-0.18631	-0.30214	-0.17247	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}\ (eV)$	0.13663 [21]	0.13663 [21]	0.08679 [42]	0.12832 [43]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}\ (eV)$	-0.18089	-0.11799	-0.25875	-0.10831	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{mag}\ (eV)$	0.14803	0.14803	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(_{Group})\ (eV)$	-33.26541	-33.40711	-32.82330	-126.97472	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(_{c_4\ AO/HO})\ (eV)$	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(_{c_5\ AO/HO})\ (eV)$	0	0	0	-1.16125	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(_{Group})\ (eV)$	3.99563	4.13733	3.55352	8.61994	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.187. The total bond energies of alkyl sulfates calculated using the functional group composition and the energies of Table 15.186 compared to the experimental values [3].

Formula	Name	$C-O$ (i) Group	$C-O$ (ii) Group	$O-S$ Group	SO_2 Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_2H_6SO_4$	Dimethyl sulfate	2	0	2	1	2	0	0	0	0	0	0	0	0	48.70617	48.734	0.00058
$C_4H_{10}SO_4$	Diethyl sulfate	0	2	2	1	2	2	0	2	0	0	0	0	0	73.30077	73.346	0.00061
$C_6H_{14}SO_4$	Dipropyl sulfate	0	2	2	1	2	4	0	4	0	0	0	0	0	97.61617	97.609	-0.00008

Table 15.188. The bond angle parameters of alkyl sulfates and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom, msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle O_aSO_b$	2.72654	2.72654	4.7329	-15.95954 O_a	9	-15.95954 O_b	9	0.85252	0.85252	1	1	1	0.85252	-1.65376				120.44	120.9 [44] (dimethyl sulfate)
$\angle O_aSO_c$	2.72654	2.96203	4.6690	-15.95954 O_a	9	-16.11722 O_c	11	0.85252	0.84418	1	1	1	0.84835	-1.65376				110.26	109.67 [44] (dimethyl sulfate)
$\angle O_cSO_d$	2.96203	2.96203	4.6476	-16.11722 O_c	11	-16.11722 O_d	11	0.84418	0.84418	1	1	1	0.84418	-1.65376				103.35	103.85 [44] (dimethyl sulfate)
$\angle C_aO_cS$	2.68862	2.96203	4.8416	-15.75493 C_a	7	-10.36001 S	S	0.86359	0.77641 (Eq. (15.139))	1	0.77641 (Eq. (15.139))	1	0.82000	-0.72457				117.84	117.43[44] (dimethyl sulfate)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

NITROALKANES ($C_nH_{2n+2-m}(NO_2)_m$, $n=1,2,3,4,5...\infty$)

The nitroalkanes, $C_nH_{2n+2-m}(NO_2)_m$, comprise a NO_2 functional group and a $C-N$ functional group. The alkyl portion of the nitroalkane may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in nitroalkanes are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is $1s^2 2s^2 2p^4$, and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state $^3P_2$. The electron configuration of nitrogen is $1s^2 2s^2 2p^3$, and the orbital arrangement given by Eq. (10.134) has three unpaired electrons corresponding to the ground state $^4S^0_{3/2}$. The bonding in the nitro (NO_2) functional group is similar to that in the SO_2 group given previously. It also has similarities to the bonding in the carbonyl functional group. In the NO_2 group, the two unpaired electrons of the O atoms form a MO with two unpaired electrons of the nitrogen atom such that the MO comprises a linear combination of two bonds, each of bond order two involving the nitrogen AOs and oxygen AOs of both oxygen atoms. The nitrogen atom is then energy matched to the $C2sp^3$ HO. In nitroalkanes, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3)=-14.63489\ eV$ (Eq. (15.25)), the N AO has an energy of $E(N)=-14.53414\ eV$, and the O AO has an energy of $E(O)=-13.61806\ eV$ [38]. To meet the equipotential condition of the union of the $N=O$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the $N=O$-bond MO given by Eqs. (15.68) and (15.70) is

$$\begin{aligned} c_2(O\ to\ N2p\ to\ C2sp^3HO) &= \frac{E(O)}{E(N)} c_2(C2sp^3HO) \\ &= \frac{-13.61806\ eV}{-14.53414\ eV}(0.91771) \\ &= 0.85987 \end{aligned} \tag{15.140}$$

Since there are two O atoms in a linear combination that comprises the bonding of the NO_2 group, the unpaired electrons of each O cancel each others effect such that E_{mag} is not subtracted from the total energy of NO_2. Additionally, $E_T\left(atom-atom,msp^3.AO\right)=-3.71673\ eV=4\left(-0.92918\ eV\right)$ (Eq. (14.513)) is the maximum given the bonding involves four electrons comprising two bonds, each having a bond order of one.

The $C-N$ group is equivalent to that of primary amines except that the energies corresponding to vibration in the transition state are matched to a nitroalkane and $\Delta E_{H_2MO}\left(AO/HO\right)=-0.72457\ eV$ for nitroalkane and $\Delta E_{H_2MO}\left(AO/HO\right)=-1.44915\ eV$ for primary amines. Whereas, $E_T\left(atom-atom,msp^3.AO\right)=-1.44915\ eV$ for both functional groups. This condition matches the energy of the $C-N$ group with the NO_2 having $\Delta E_{H_2MO}\left(AO/HO\right)=0$.

The symbols of the functional groups of branched-chain nitroalkanes are given in Table 15.189. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of nitroalkanes are given in Tables 15.190, 15.191, and 15.192, respectively. The total energy of each nitroalkane given in Table 15.193 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.192 corresponding to functional-group composition of the molecule. E_{mag} given by Eq. (15.58) was subtracted for each t-butyl group. The bond angle parameters of nitroalkanes determined using Eqs. (15.79-15.108) are given in Table 15.194.

Table 15.189. The symbols of functional groups of nitroalkanes.

Functional Group	Group Symbol
NO_2 group	NO_2
C-N	$C-N$
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.190. The geometrical bond parameters of nitroalkanes and experimental values [1].

Parameter	NO_2 Group	$C-N$ Group	$C-H$ (CH_3) Group	$C-H$ (CH_2) Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
a (a_0)	1.33221	1.97794	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
c' (a_0)	1.15421	1.40639	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ $(Å)$	1.22157	1.48846	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(Å)$	1.224 (nitromethane)	1.489 (nitromethane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
b,c (a_0)	0.66526	1.39079	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.86639	0.71104	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.191. The MO to HO intercept geometrical bond parameters of nitroalkanes. R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$RN(O)=O$	O	-0.92918	0	0	0		1.00000	0.86359	-15.75493		135.25	44.75	66.05	0.54089	0.61333
$RN(O)=O$	N	-0.92918	-0.92918	-0.72457	0		0.93084	0.78155	-17.40869		131.57	48.43	61.50	0.63558	0.51864
H_3C-NO_2	C	-0.72457	0	0	0	-152.34026	0.91771	0.87495	-15.55033	-15.35946	80.47	99.53	38.35	1.55123	0.14484
RH_2C-NO_2 $R=H,alkyl$	N	-0.92918	-0.92918	-0.72457	0		0.93084	0.78155	-17.40869		69.30	110.70	31.71	1.68259	0.27620
$-H_2C_\alpha-NO_2$	C_α	-0.72457	-0.92918	0	0	-153.26945	0.91771	0.82562	-16.47951	-16.28864	74.96	105.04	34.98	1.62061	0.21422
$C-H$ (CH_3)	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H$ (CH_2)	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H$ (CH)	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.192. The energy parameters (eV) of functional groups of nitroalkanes.

Parameters	NO_2 Group	$C-N$ Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	2	1	3	2	1	1	1	1	1	1	1
n_2	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1
c_2	0.85987	0.91140	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	0	1	1	0	0	0	1	1	0
c_4	4	2	1	1	1	2	2	2	2	2	2
c_5	0	0	3	2	1	0	0	0	0	0	0
C_{1o}	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	1	1	1	1	1	1	1	1	1	1	1
V_e (eV)	-106.90919	-31.36351	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	23.57588	9.67426	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	40.12475	7.92833	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_m (eV)	-20.06238	-3.96416	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(_{AO/HO})$ (eV)	0	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(_{AO/HO})$ (eV)	0	-0.72457	0	0	0	0	0	0	0	0	0
$E_T(_{AO/HO})$ (eV)	0	-13.91032	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(_{H_2MO})$ (eV)	-63.27093	-31.63540	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom, msp^3.AO)$ (eV)	-3.71673	-1.44915	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(_{MO})$ (eV)	-66.98746	-33.08452	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω $(10^{15}$ $rad/s)$	19.0113	10.5087	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	12.51354	6.91703	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D$ (eV)	-0.23440	-0.17214	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}$ (eV)	0.19342 [45]	0.10539 [45]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}$ (eV)	-0.13769	-0.11945	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mag} (eV)	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(_{Group})$ (eV)	-67.26284	-33.20397	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(_{c_4\ AO/HO})$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(_{c_5\ AO/HO})$ (eV)	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(_{Group})$ (eV)	8.72329	3.93419	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.193. The total bond energies of nitroalkanes calculated using the functional group composition and the energies of Table 15.192 compared to the experimental values [3]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(_{Group})$ (eV) values based on composition is given by (15.58).

Formula	Name	NO_2 Group	$C-N$ Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_3NO_2	Nitromethane	1	1	1	0	0	0	0	0	0	0	0	0	25.14934	25.107	-0.00168
$C_2H_5NO_2$	Nitroethane	1	1	1	1	0	1	0	0	0	0	0	0	37.30704	37.292	-0.00040
$C_3H_7NO_2$	1-Nitropropane	1	1	1	2	0	2	0	0	0	0	0	0	49.46474	49.451	-0.00028
$C_3H_7NO_2$	2-Nitropropane	1	1	2	0	1	0	2	0	0	0	0	0	49.56563	49.602	0.00074
$C_4H_9NO_2$	1-Nitrobutane	1	1	1	3	0	3	0	0	0	0	0	0	61.62244	61.601	-0.00036
$C_4H_9NO_2$	2-Nitroisobutane	1	1	3	0	0	0	0	3	0	0	0	-1	61.90697	61.945	0.00061
$C_5H_{11}NO_2$	1-Nitropentane	1	1	1	4	0	4	0	0	0	0	0	0	73.78014	73.759	-0.00028

Table 15.194. The bond angle parameters of nitroalkanes and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ or E Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle NC_aH$	2.81279	2.09711	3.9665	-14.82575	1	-14.53414	N	0.91771	0.91140 (Eq. (15.116))	0.75	1	0.75	0.99312	0				106.87	107 (nitromethane)
$\angle O_aNO_b$	2.30843	2.30843	4.1231	-16.68411 O_a	24	-16.68411 O_b	24	0.81549	0.81549	1	1	1	0.81549	-1.44915				126.52	125.3 (nitromethane)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$																			
$\angle C_aC_bH$															70.56			109.44	
															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

ALKYL NITRITES ($C_nH_{2n+2-m}(NO_2)_m$, $n = 1,2,3,4,5...\infty$)

The alkyl nitrites, $C_nH_{2n+2-m}(NO_2)_m$, comprise a $RC-O-NO$ moiety that comprises $C-O$, $O-N$, and NO functional groups. The alkyl portion of the alkyl nitrite may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in alkyl nitrites are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is $1s^2 2s^2 2p^4$, and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state $^3P_2$. The electron configuration of nitrogen is $1s^2 2s^2 2p^3$, and the orbital arrangement given by Eq. (10.134) has three unpaired electrons corresponding to the ground state $^4S^0_{3/2}$. The bonding in the nitro (NO) functional group is similar to that in the SO group given previously. It also has similarities to the bonding in the carbonyl functional group. In the NO group, the two unpaired electrons of the O atom form a MO with two unpaired electrons of the nitrogen atom such that the MO comprises a double bond. The nitrogen atom is then energy matched to the $O-N$ functional group that is further energy matched to the $C2sp^3$ HO of the $C-O$ functional group. To meet the equipotential condition of the union of the $N=O$ H_2-type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor c_2 of Eq. (15.51) for the $N=O$-bond MO given by Eq. (15.140) is $c_2(O\ to\ N2p\ to\ C2sp^3HO) = 0.85987$.

As in the case of the carbonyl group, two unpaired O electrons result upon bond breakage of the $N=O$ bond which requires that two times E_{mag} of oxygen (Eq. (15.59)) be subtracted from the total energy of NO. Additionally, $E_T(atom-atom, msp^3.AO)$ and $\Delta E_{H_2MO}(AO/HO)$ are equal to $-0.92918\ eV$ (Eq. (14.513)) which matches the energy of the $N=O$ bond with the contiguous $O-N$ bond and matches the energy contribution of an oxygen atom.

The $O-N$ functional group comprise a single-bond, H_2-type-ellipsoidal-MO between the remaining unpaired nitrogen electron and an unpaired electron of the second oxygen atom which further forms a single bond with the $C2sp^3$ HO of the $C-O$ functional group. In alkyl nitrites, the hybridization factor c_2 of Eq. (15.52) for the $C-O$-bond MO given by Eq. (15.114) is $c_2\left(C2sp^3HO \ to \ O\right)=0.85395$. The hybridization factor c_2 of Eq. (15.52) for a $C-N$-bond MO given by Eq. (15.116) is $c_2\left(C2sp^3HO \ to \ N\right)=0.91140$. Thus, the hybridization factor c_2 of Eq. (15.52) for $O-N$ that bridges the $C-O$ and $N=O$ bonds given by Eq. (15.69) is

$$c_2(N2p \ to \ O2p)=\frac{c_2\left(C2sp^3HO \ to \ N\right)}{c_2\left(C2sp^3HO \ to \ O\right)}=\frac{0.91140}{0.85395}=1.06727 \qquad (15.141)$$

$E_T\left(atom-atom,msp^3.AO\right)=-0.92918 \ eV$ in order to match the energy of the NO group and $E\left(AO/HO\right)=-15.35946 \ eV$ in order to match the $C-O$ functional group.

The $C-O$ functional group is equivalent to that of an ether as given in the corresponding section except that $E_T\left(atom-atom,msp^3.AO\right)$ and $\Delta E_{H_2MO}\left(AO/HO\right)$ are both $-0.72457 \ eV$ which matches the energy contribution of an independent $C2sp^3$ HO (Eq. (14.151)). Also, the energy terms corresponding to the oscillation of the bond in the transition state are matched to a nitrite.

The symbols of the functional groups of branched-chain alkyl nitrites are given in Table 15.195. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl nitrites are given in Tables 15.196, 15.197, and 15.198, respectively. The total energy of each alkyl nitrite given in Table 15.199 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.198 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl nitrites determined using Eqs. (15.79-15.108) are given in Table 15.200.

Table 15.195. The symbols of functional groups of alkyl nitrites.

Functional Group	Group Symbol
NO group	NO
O-N	$O-N$
C-O	$C-O$
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.196. The geometrical bond parameters of alkyl nitrites and experimental values [1].

Parameter	NO Group	$O-N$ Group	$C-O$ Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.32255	1.76440	1.85327	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.15002	1.32831	1.36135	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ (Å)	1.21713	1.40582	1.44079	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.205 (methyl nitrate) 1.2 (HNO_2)	1.402 (methyl nitrate) 1.432 (HNO_2)	1.437 (methyl nitrate)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	0.65314	1.16134	1.25751	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.86955	0.75284	0.73457	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.197. The MO to HO intercept geometrical bond parameters of alkyl nitrites. R, R', R'' are H or alkyl groups. E_T is $E_T(atom-atom, msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$RON=O$	O	-0.46459	0	0	0		1.00000	0.88983	-15.29034		137.15	42.85	67.90	0.49764	0.65238
$RON=O$	N	-0.46459	-0.46459	0	0		0.93084	0.86359	-15.75493		136.09	43.91	66.48	0.52781	0.62221
RO_b-NO_a	O_b	-0.46459	-0.36229	0	0		1.00000	0.86923	-15.65263		99.22	80.78	47.63	1.18905	0.13925
RO_b-NO_a	N	-0.46459	-0.46459	0	0		0.93084	0.86359	-15.75493		98.78	81.22	47.30	1.19655	0.13175
$RH_2C_a-O_bNO_a$ $R=H, alkyl$	O_b	-0.36229	-0.46459	0	0		1.00000	0.86923	-15.65263		91.43	88.57	43.71	1.33962	0.02173
$H_3C_a-O_bNO_a$	C_a	-0.36229	0	0	0	-151.97798	0.91771	0.89582	-15.18804	-14.99717	93.71	86.29	45.31	1.30342	0.05793
$-CH_2H_2C_a-O_bNO_a$	C_a	-0.36229	-0.92918	0	0	-152.90716	0.91771	0.84418	-16.11722	-15.92636	89.16	90.84	42.16	1.37373	0.01238
$C-H\ (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\ (CH)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ $(C-C\ (a))$	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ $(C-C\ (a))$	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b(H_2C_c-R')HCH_2-$ $(C-C\ (b))$	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C\ (c))$	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b(H_2C_c-R')HCH_2-$ $(C-C\ (d))$	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C\ (e))$	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b(H_2C_c-R')HCH_2-$ $(C-C\ (f))$	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C\ (f))$	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.198. The energy parameters (eV) of functional groups of alkyl nitrites.

Parameters	NO Group	$O-N$ Group	$C-O$ Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	2	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1	1
c_2	0.85987	1.06727	0.85395	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	2	0	0	0	1	1	0	0	0	1	1	0
c_4	4	2	2	1	1	1	2	2	2	2	2	2
c_5	0	0	0	3	2	1	0	0	0	0	0	0
C_{1o}	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	1	1	1	1	1	1	1	1	1	1	1	1
V_e (eV)	-108.34117	-42.83043	-32.04173	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	23.66182	20.48593	9.99436	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	40.95920	12.13739	8.64465	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_m (eV)	-20.47960	-6.06870	-4.32232	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(_{AO/HO})$ (eV)	0	-15.35946	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(_{AO/HO})$ (eV)	-0.92918	0	-0.72457	0	0	0	0	0	0	0	0	0
$E_T(_{AO/HO})$ (eV)	0.92918	-15.35946	-13.91032	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(_{H_2MO})$ (eV)	-63.27057	-31.63527	-31.63537	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom, msp^3.AO)$ (eV)	-0.92918	-0.92918	-0.72457	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(_{MO})$ (eV)	-64.19992	-32.56455	-32.35994	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω $(10^{15}\ rad/s)$	19.2199	23.3578	20.7301	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	12.65089	15.37450	13.64490	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D$ (eV)	-0.22587	0.25261	-0.23648	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}$ (eV)	0.20396 [46]	0.10725 [47]	0.13663 [21]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}$ (eV)	-0.12390	0.19899	-0.16817	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mag} (eV)	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(_{Group})$ (eV)	-64.44771	32.76354	-32.52811	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(_{c_4\ AO/HO})$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(_{c_5\ AO/HO})$ (eV)	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(_{Group})$ (eV)	5.67933	3.49376	3.25833	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.199. The total bond energies of alkyl nitrites calculated using the functional group composition and the energies of Table 15.198 compared to the experimental values [3].

Formula	Name	NO Group	$O-N$ Group	$C-O$ Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_3NO_2	Methyl nitrite	1	1	1	1	0	0	0	0	0	0	0	0	24.92328	24.955	0.00126

Table 15.200. The bond angle parameters of alkyl nitrites and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom, msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ or E Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CO_bN$	2.72270	2.65661	4.4944	-16.68412 C_b	25	-14.53414 N	N	0.81549	0.91140 (Eq. (15.116))	1	1	1	0.86345	-1.44915				113.33	
$\angle O_aNO_b$	2.30004	2.65661	4.1231	-16.68411 O_a	24	-16.68411 O_b	24	0.81549	0.81549	1	1	1	0.81549	-1.44915				112.38	110.7 (HNO_2)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

ALKYL NITRITES ($C_nH_{2n+2-m}(NO_2)_m$, $n=1,2,3,4,5...\infty$)

The alkyl nitrites, $C_nH_{2n+2-m}(NO_2)_m$, comprise a $RC-O-NO$ moiety that comprises $C-O$, $O-N$, and NO functional groups. The alkyl portion of the alkyl nitrite may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in alkyl nitrites are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is $1s^22s^22p^4$, and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state $^3P_2$. The electron configuration of nitrogen is $1s^22s^22p^3$, and the orbital arrangement given by Eq. (10.134) has three unpaired electrons corresponding to the ground state $^4S^0_{3/2}$. The bonding in the nitro (NO) functional group is similar to that in the SO group given previously. It also has similarities to the bonding in the carbonyl functional group. In the NO group, the two unpaired electrons of the O atom form a MO with two unpaired electrons of the nitrogen atom such that the MO comprises a double bond. The nitrogen atom is then energy matched to the $O-N$ functional group that is further energy matched to the $C2sp^3$ HO of the $C-O$ functional group. To meet the equipotential condition of the union of the $N=O$ H_2-type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor c_2 of Eq. (15.51) for the $N=O$-bond MO given by Eq. (15.140) is $c_2(O\ to\ N2p\ to\ C2sp^3HO)=0.85987$.

As in the case of the carbonyl group, two unpaired O electrons result upon bond breakage of the $N=O$ bond which requires that two times E_{mag} of oxygen (Eq. (15.59)) be subtracted from the total energy of NO. Additionally, $E_T(atom-atom,msp^3.AO)$ and $\Delta E_{H_2MO}(AO/HO)$ are equal to $-0.92918\ eV$ (Eq. (14.513)) which matches the energy of the $N=O$ bond with the contiguous $O-N$ bond and matches the energy contribution of an oxygen atom.

The $O-N$ functional group comprise a single-bond, H_2-type-ellipsoidal-MO between the remaining unpaired nitrogen electron and an unpaired electron of the second oxygen atom which further forms a single bond with the $C2sp^3$ HO of the $C-O$ functional group. In alkyl nitrites, the hybridization factor c_2 of Eq. (15.52) for the $C-O$-bond MO given by Eq. (15.114) is $c_2(C2sp^3HO\ to\ O)=0.85395$. The hybridization factor c_2 of Eq. (15.52) for a $C-N$-bond MO given by Eq. (15.116) is $c_2(C2sp^3HO\ to\ N)=0.91140$. Thus, the hybridization factor c_2 of Eq. (15.52) for $O-N$ that bridges the $C-O$ and $N=O$ bonds given by Eq. (15.69) is

$$c_2(N2p\ to\ O2p)=\frac{c_2(C2sp^3HO\ to\ N)}{c_2(C2sp^3HO\ to\ O)}=\frac{0.91140}{0.85395}=1.06727 \qquad (15.141)$$

$E_T(atom-atom,msp^3.AO)=-0.92918\ eV$ in order to match the energy of the NO group and $E(AO/HO)=-15.35946\ eV$ in order to match the $C-O$ functional group.

The $C-O$ functional group is equivalent to that of an ether as given in the corresponding section except that $E_T(atom-atom,msp^3.AO)$ and $\Delta E_{H_2MO}(AO/HO)$ are both $-0.72457\ eV$ which matches the energy contribution of an independent $C2sp^3$ HO (Eq. (14.151)). Also, the energy terms corresponding to the oscillation of the bond in the transition state are matched to a nitrite.

The symbols of the functional groups of branched-chain alkyl nitrites are given in Table 15.195. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl nitrites are given in Tables 15.196, 15.197, and 15.198, respectively. The total energy of each alkyl nitrite given in Table 15.199 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.198 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl nitrites determined using Eqs. (15.79-15.108) are given in Table 15.200.

Table 15.195. The symbols of functional groups of alkyl nitrites.

Functional Group	Group Symbol
NO group	NO
O-N	$O-N$
C-O	$C-O$
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (*n*-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.196. The geometrical bond parameters of alkyl nitrites and experimental values [1].

Parameter	NO Group	$O-N$ Group	$C-O$ Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.32255	1.76440	1.85327	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.15002	1.32831	1.36135	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (Å)$	1.21713	1.40582	1.44079	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(Å)$	1.205 (methyl nitrate) 1.2 (HNO_2)	1.402 (methyl nitrate) 1.432 (HNO_2)	1.437 (methyl nitrate)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b, c\ (a_0)$	0.65314	1.16134	1.25751	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.86955	0.75284	0.73457	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.197. The MO to HO intercept geometrical bond parameters of alkyl nitrites. R, R', R'' are H or alkyl groups. E_T is $E_T(atom-atom, msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$RON=O$	O	-0.46459	0	0	0		1.00000	0.88983	-15.29034		137.15	42.85	67.90	0.49764	0.65238
$RON=O$	N	-0.46459	-0.46459	0	0		0.93084	0.86359	-15.75493		136.09	43.91	66.48	0.52781	0.62221
RO_b-NO_a	O_b	-0.46459	-0.36229	0	0		1.00000	0.86923	-15.65263		99.22	80.78	47.63	1.18905	0.13925
RO_b-NO_a	N	-0.46459	-0.46459	0	0		0.93084	0.86359	-15.75493		98.78	81.22	47.30	1.19655	0.13175
$RH_2C_a-O_bNO_a$ $R=H, alkyl$	O_b	-0.36229	-0.46459	0	0		1.00000	0.86923	-15.65263		91.43	88.57	43.71	1.33962	0.02173
$H_3C_a-O_bNO_a$	C'_a	-0.36229	0	0	0	-151.97798	0.91771	0.89582	-15.18804	-14.99717	93.71	86.29	45.31	1.30342	0.05793
$-CH_2H_2C_a-O_bNO_a$	C'_a	-0.36229	-0.92918	0	0	-152.90716	0.91771	0.84418	-16.11722	-15.92636	89.16	90.84	42.16	1.37373	0.01238
$C-H\ (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\ (CH)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C'_aC'_bH_2CH_2-$ $(C-C\ (a))$	C'_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C'_aC'_bH_2CH_2-$ $(C-C\ (a))$	C'_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C'_aC'_b(H_2C_c-R')HCH_2-$ $(C-C\ (b))$	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C'_a(R'-H_2C_d)C'_b(R''-H_2C_c)CH_2-$ $(C-C\ (c))$	C'_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC'_aC'_b(H_2C_c-R')HCH_2-$ $(C-C\ (d))$	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC'_a(R'-H_2C_d)C'_b(R''-H_2C_c)CH_2-$ $(C-C\ (e))$	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC'_aC'_b(H_2C_c-R')HCH_2-$ $(C-C\ (f))$	C'_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC'_a(R'-H_2C_d)C'_b(R''-H_2C_c)CH_2-$ $(C-C\ (f))$	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.198. The energy parameters (eV) of functional groups of alkyl nitrites.

Parameters	NO Group	$O-N$ Group	$C-O$ Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	2	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1	1
c_2	0.85987	1.06727	0.85395	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	2	0	0	0	1	1	0	0	0	1	1	0
c_4	4	2	2	1	1	1	2	2	2	2	2	2
c_5	0	0	0	3	2	1	0	0	0	0	0	0
C_{1o}	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	1	1	1	1	1	1	1	1	1	1	1	1
V_e (eV)	-108.34117	-42.83043	-32.04173	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	23.66182	20.48593	9.99436	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	40.95920	12.13739	8.64465	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_m (eV)	-20.47960	-6.06870	-4.32232	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(AO/HO)$ (eV)	0	-15.35946	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(AO/HO)$ (eV)	-0.92918	0	-0.72457	0	0	0	0	0	0	0	0	0
$E_T(AO/HO)$ (eV)	0.92918	-15.35946	-13.91032	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(H_2MO)$ (eV)	-63.27057	-31.63527	-31.63537	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom,msp^3.AO)$ (eV)	-0.92918	-0.92918	-0.72457	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(MO)$ (eV)	-64.19992	-32.56455	-32.35994	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω $(10^{15}\ rad/s)$	19.2199	23.3578	20.7301	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	12.65089	15.37450	13.64490	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D$ (eV)	-0.22587	0.25261	-0.23648	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}$ (eV)	0.20396 [46]	0.10725 [47]	0.13663 [21]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}$ (eV)	-0.12390	0.19899	-0.16817	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mag} (eV)	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(Group)$ (eV)	-64.44771	32.76354	-32.52811	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(c_4\ AO/HO)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(c_5\ AO/HO)$ (eV)	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(Group)$ (eV)	5.67933	3.49376	3.25833	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.199. The total bond energies of alkyl nitrites calculated using the functional group composition and the energies of Table 15.198 compared to the experimental values [3].

Formula	Name	NO Group	$O-N$ Group	$C-O$ Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_3NO_2	Methyl nitrite	1	1	1	1	0	0	0	0	0	0	0	0	24.92328	24.955	0.00126

Table 15.200. The bond angle parameters of alkyl nitrites and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom, msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ or E Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CO_bN$	2.72270	2.65661	4.4944	-16.68412 C_b	25	-14.53414 N	N	0.81549	0.91140 (Eq. (15.116))	1	1	1	0.86345	-1.44915				113.33	
$\angle O_aNO_b$	2.30004	2.65661	4.1231	-16.68411 O_a	24	-16.68411 O_b	24	0.81549	0.81549	1	1	1	0.81549	-1.44915				112.38	110.7 (HNO_2)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C'_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C'_aC'_bC'_c$															70.56			109.44	
$\angle C'_aC'_bH$															70.56			109.44	
$\angle C'_bC'_aC'_c$ iso C'_a	2.91547	2.91547	4.7958	-16.68412 C'_b	25	-16.68412 C'_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C'_bC'_aH$ iso C'_a	2.91547	2.11323	4.1633	-15.55033 C'_a	5	-14.82575 C'_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C'_aC'_bH$ iso C'_a	2.91547	2.09711	4.1633	-15.55033 C'_b	5	-14.82575 C'_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C'_bC'_aC'_c$ tert C'_a	2.90327	2.90327	4.7958	-15.55033 C'_b	5	-14.82575 C'_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C'_bC'_aC'_d$															72.50			107.50	

ALKYL NITRATES ($C_nH_{2n+2-m}(NO_2)_m$, $n=1,2,3,4,5...\infty$)

The alkyl nitrates, $C_nH_{2n+2-m}(NO_3)_m$, comprise a $RC-O-NO_2$ moiety that comprises $C-O$, $O-N$, and NO_2 functional groups. The alkyl portion of the alkyl nitrate may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in alkyl nitrates are equivalent to those in branched-chain alkanes.

The NO_2 functional group is equivalent to that of nitro alkanes with the exception that $\Delta E_{H_2MO}(AO/HO)$ as well as $E_T(atom-atom,msp^3.AO)$ is equal to $-3.71673\ eV$ in order to match the group energy to that of the contiguous $O-N$ bond. Furthermore, the $O-N$ group with $E_T(atom-atom,msp^3.AO)=-0.92918\ eV$ is equivalent to that of nitrites as given in the corresponding section.

The $C-O$ functional group is equivalent to that of an ether as given in the corresponding section except that $E_T(atom-atom,msp^3.AO)$ and $\Delta E_{H_2MO}(AO/HO)$ are both $-0.92918\ eV$ which matches the energy contribution of an independent $C2sp^3$ HO (Eq. (14.513)). Also, the energy terms corresponding to the oscillation of the bond in the transition state are matched to a nitrate.

The symbols of the functional groups of branched-chain alkyl nitrates are given in Table 15.201. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl nitrates are given in Tables 15.202, 15.203, and 15.204, respectively. The total energy of each alkyl nitrate given in Table 15.205 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.204 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl nitrates determined using Eqs. (15.79-15.108) are given in Table 15.206.

Table 15.201. The symbols of functional groups of alkyl nitrates.

Functional Group	Group Symbol
NO_2 group	NO_2
O-N	$O-N$
C-O	$C-O$
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.202. The geometrical bond parameters of alkyl nitrates and experimental values [1].

Parameter	NO_2 Group	$O-N$ Group	$C-O$ Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.29538	1.76440	1.83991	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.13815	1.32831	1.35643	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ ($\AA$)	1.20456	1.40582	1.43559	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length ($\AA$)	1.205 (methyl nitrate) 1.2 (HNO_2)	1.402 (methyl nitrate) 1.432 (HNO_2)	1.437 (methyl nitrate)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	0.61857	1.16134	1.24312	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.87862	0.75284	0.73723	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.203. The MO to HO intercept geometrical bond parameters of alkyl nitrates. R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' $(^\circ)$	θ_1 $(^\circ)$	θ_2 $(^\circ)$	d_1 (a_0)	d_2 (a_0)
$RN(O)=O$	O	-0.92918	0	0	0		1.00000	0.86359	-15.75493		138.49	41.51	67.70	0.49144	0.64671
$RN(O)=O$	N	-0.92918	-0.92918	-0.46459	0		0.93084	0.79340	-17.14870		135.60	44.40	63.83	0.57133	0.56682
$RO_b-N(O_a)_2$	O_b	-0.46459	-0.46459	0	0		1.00000	0.86359	-15.75493		98.78	81.22	47.30	1.19655	0.13175
$RO_b-N(O_a)_2$	N	-0.46459	-0.92918	-0.92918	0		0.93084	0.79340	-17.14870		92.78	87.22	43.03	1.28978	0.03852
$RH_2C_a-O_bN(O_a)_2$ $R=H,alkyl$	O_b	-0.46459	-0.46459	0	0		1.00000	0.86359	-15.75493		92.13	87.87	43.96	1.32431	0.03212
$H_3C_a-O_bN(O_a)_2$	C_a	-0.46459	0	0	0	-152.08028	0.91771	0.88983	-15.29034	-15.09948	94.36	85.64	45.54	1.28872	0.06771
$-CH_2H_2C_a-O_bN(O_a)_2$	C_a	-0.46459	-0.92918	0	0	-153.00946	0.91771	0.83885	-16.21952	-16.02866	89.90	90.10	42.44	1.35787	0.00143
$C-H\ (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\ (CH)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ $(C-C\ (a))$	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ $(C-C\ (a))$	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b(H_2C_c-R')HCH_2-$ $(C-C\ (b))$	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C\ (c))$	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b(H_2C_c-R')HCH_2-$ $(C-C\ (d))$	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C\ (e))$	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b(H_2C_c-R')HCH_2-$ $(C-C\ (f))$	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C\ (f))$	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.204. The energy parameters (eV) of functional groups of alkyl nitrates.

Parameters	NO_2 Group	$O-N$ Group	$C-O$ Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	2	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1	1
c_2	0.85987	1.06727	0.85395	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	0	0	1	1	0	0	0	1	1	0
c_4	4	2	2	1	1	1	2	2	2	2	2	2
c_5	0	0	0	3	2	1	0	0	0	0	0	0
C_{1o}	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	1	1	1	1	1	1	1	1	1	1	1	1
V_e (eV)	-112.63415	-42.83043	-32.35681	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	23.90868	20.48593	10.03058	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	43.47534	12.13739	8.79304	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_m (eV)	-21.73767	-6.06870	-4.39652	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(_{AO/HO})$ (eV)	0	-15.35946	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(_{AO/HO})$ (eV)	-3.71673	0	-0.92918	0	0	0	0	0	0	0	0	0
$E_T(_{AO/HO})$ (eV)	3.71673	-15.35946	-13.70571	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(_{H_2MO})$ (eV)	-63.27107	-31.63527	-31.63542	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T\left(atom-atom,msp^3.AO\right)$ (eV)	-3.71673	-0.92918	-0.92918	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(_{MO})$ (eV)	-66.98746	-32.56455	-32.56455	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω $\left(10^{15}\ rad/s\right)$	19.8278	23.3578	21.0910	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	13.05099	15.37450	13.88249	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D$ (eV)	-0.23938	0.25261	-0.24004	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}$ (eV)	0.19342 [45]	0.10725 [47]	0.13663 [21]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}$ (eV)	-0.14267	0.19899	-0.17172	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mag} (eV)	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(_{Group})$ (eV)	-67.27281	32.76354	-32.73627	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(_{c_4\ AO/HO})$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(_{c_5\ AO/HO})$ (eV)	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(_{Group})$ (eV)	8.73325	3.49376	3.46649	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.205. The total bond energies of alkyl nitrates calculated using the functional group composition and the energies of Table 15.204 compared to the experimental values [3].

Formula	Name	NO_2 Group	$O-N$ Group	$C-O$ Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_3NO_3	Methyl nitrate	1	1	1	1	0	0	0	0	0	0	0	0	28.18536	28.117	-0.00244
$C_2H_5NO_3$	Ethyl nitrate	1	1	1	1	1	0	1	0	0	0	0	0	40.34306	40.396	0.00131
$C_3H_7NO_3$	Propyl nitrate	1	1	1	1	2	1	2	0	0	0	0	0	52.50076	52.550	0.00093
$C_3H_7NO_3$	Isopropyl nitrate	1	1	1	2	0	1	0	2	0	0	0	0	52.60165	52.725	0.00233

Table 15.206. The bond angle parameters of alkyl nitrates and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom, msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ or E Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle H_aC_aO_c$															70.56			109.44	110 (methyl nitrate)
$\angle H_bC_aO_c$	2.09711	2.71287	3.7238	-14.82575 C_a	1	-13.61806	O	0.91771	0.85395 (Eq. (15.114))	0.75	1	0.75	0.93052	0				100.68	103 (methyl nitrate)
$\angle O_aNO_b$	2.27630	2.27630	4.1231	-16.68411 O_a	24	-16.68411 O_b	24	0.81549	0.81549	1	1	1	0.81549	-1.44915				129.83	
$\angle O_aNO_c$																129.83		115.09 (Eq. (15.99))	118.1 (methyl nitrate)
$\angle O_bNO_c$																129.83		115.09 (Eq. (15.99))	112.4 (methyl nitrate)
$\angle CO_cN$	2.71287	2.65661	4.4721	-16.68412 C_b	25	-14.53414 N	N	0.81549	0.91140 (Eq. (15.116))	1	1	1	0.86345	-1.44915				112.79	112.7 (methyl nitrate)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

CYCLIC AND CONJUGATED ALKENES

($C_nH_{2n+2-2m-2c}$, $n = 3,4,5...\infty$, $m = 1,2,3...$, $c = 0$ or 1)

The cyclic and conjugated alkenes are represented by the general formula $C_nH_{2n+2-2m-2c}$, $n = 3,4,5...\infty$, $m = 1,2,3...$, $c = 0$ or 1 where m is the number of double bonds and $c = 0$ for a straight-chain alkene and $c = 1$ for a cyclic alkene. They have at least one carbon-carbon double bond comprising a functional group that is solved equivalently to the double bond of ethylene. Consider the cyclic and conjugated alkenes 1,3-butadiene, 1,3-pentadiene, 1,4-pentadiene, 1,3-cyclopentadiene, and cyclopentene. Based on the condition of energy matching of the orbital, any magnetic energy due to unpaired electrons in the constituent fragments, and differences in oscillation in the transition state, five distinct $C-C$ functional groups can be identified as given in Table 15.208. The designation of the structure of the groups are shown in Figures 61A-E. In addition, CH_2 of any $-C=CH_2$ moiety is an conjugated alkene functional group. The alkyl portion of the cyclic or conjugated alkene may comprise at least one terminal methyl group (CH_3), and may comprise methylene (CH_2), and methylyne (CH) functional groups that are equivalent to those of branched-chain alkanes.

The solution of the functional groups comprises the hybridization of the $2s$ and $2p$ AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. The $C-C$ groups are solved in the same manner as those of the branched-chain alkanes given in the corresponding section. For example, the cyclopentene C_a-C_b group is equivalent to the n-$C-C$ alkane group. Many of the corresponding energies of the molecules of this class are similar, and they can be related to one another based on the structure. For example, cyclopentadiene is formed by ring closure of 1,3-pentadiene with the elimination of H from the terminal methyl and methylene groups. Thus, the energy of each of the corresponding carbon-carbon bonds in cyclopentadiene is the same as that in 1,3-pentadiene except that the difference between the energies of the 1,3-pentadiene C_c-C_d and the cyclopentadiene C_a-C_b groups is the magnetic energy (Eq. (15.58)) which is subtracted from the C_a-C_b total bond energy according to Eqs. (13.524-13.527) due to the formation of a CH group from the methylene group.

$E_T\left(atom-atom,msp^3.AO\right)$ of the $C=C$-bond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is equivalent to that of ethylene, $-2.26759\ eV$, given by

Eq. (14.247). $E_T\left(atom-atom,msp^3.AO\right)$ of each $C-C$-bond MO in Eq. (15.52) is $-2.26759\ eV$ or $-1.85836\ eV$ based on the energy match between the $C2sp^3$ HOs corresponding to the energy contributions equivalent to those of alkene, $-1.13379\ eV$ (Eq. (14.247)), or methylene, $-0.92918\ eV$ (Eq. (14.513)), groups, respectively, that are contiguous with the $C-C$-bond carbons. In the former case, the total energy of the $C-C$ bond MO is matched to that of the alkane energy in the determination of the bond length. The charge density of 0.5e must be donated to the $C-C$ bond in order to match the energy of the adjacent flanking double bonds. This further lowers the total energy of the $C-C$-bond MO and increases the $C-C$ bond energy. This additional lowering of the $C-C$-bond energy by additional charge donation over that of an alkane bond due to adjacent double bonds is called *conjugation.*

The symbols of the functional groups of cyclic and conjugated alkenes are given in Table 15.207. The structures of 1,3-butadiene, 1,3-pentadiene, 1,4-pentadiene, 1,3-cyclopentadiene, and cyclopentene are shown in Figures 61A-E, respectively. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of cyclic and conjugated alkenes are given in Tables 15.208, 15.209, and 15.210, respectively. The total energy of each cyclic or conjugated alkenes given in Table 15.211 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.210 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage , the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of cyclic and conjugated alkenes determined using Eqs. (15.79-15.108) are given in Table 15.212.

Table 15.207. The symbols of functional groups of cyclic and conjugated alkenes.

Functional Group	Group Symbol
CC double bond	$C=C$
1,3-butadiene, 1,3-pentadiene C_b-C_b 1,3-cyclopentadiene C_c-C_c	$C-C$ (a)
1,3-pentadiene C_c-C_d cyclopentene C_b-C_c	$C-C$ (b)
1,4-pentadiene C_b-C_c	$C-C$ (c)
1,3-cyclopentadiene C_a-C_b	$C-C$ (d)
cyclopentene C_a-C_b	$C-C$ (e)
CH_2 alkenyl group	$C-H\ (CH_2)$ (i)
CH_3 group	$C-H\ (CH_3)$
CH_2 alkyl group	$C-H\ (CH_2)$ (ii)
CH	$C-H$

Table 15.208. The geometrical bond parameters of cyclic and conjugated alkenes and experimental values [1].

Parameter	$C=C$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-H\ (CH_2)$ (i) Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ (ii) Group	$C-H$ Group
$a\ (a_0)$	1.47228	1.91256	2.04740	2.04740	2.04740	2.12499	1.64010	1.64920	1.67122	1.67465
$c'\ (a_0)$	1.26661	1.38295	1.43087	1.43087	1.43087	1.45773	1.04566	1.04856	1.05553	1.05661
Bond Length $2c'$ ($\AA$)	1.34052	1.46365	1.51437	1.51437	1.51437	1.54280	1.10668	1.10974	1.11713	1.11827
Exp. Bond Length ($\AA$)	1.349 (1,3-butadiene) 1.342 (1,3-cyclopentadiene) 1.342 (cyclopentene)	1.467 (1,3-butadiene) 1.469 (1,3-cyclopentadiene)	1.519 (cyclopentene)		1.509 (1,3-cyclopentadiene)	1.546 (cyclopentene)	1.10 (2-methylpropene) 1.108 (avg.) (1,3-butadiene)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)
$b,c\ (a_0)$	0.75055	1.32110	1.46439	1.46439	1.46439	1.54615	1.26354	1.27295	1.29569	1.29924
e	0.86030	0.72309	0.69887	0.69887	0.69887	0.68600	0.63756	0.63580	0.63159	0.63095

Table 15.209. The MO to HO intercept geometrical bond parameters of cyclic and conjugated alkenes R_1 is an alkyl group and R, R', R'' are H or alkyl groups. E_T is $E_T(atom-atom, msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$H_2C_a=C_b(H)(H)C=CR$ (1,3-butadiene, 1,3-pentadiene) $H_2C_a=C_b(H)C_cH_2C_b(H)=C_aH_2$ (1,4-pentadiene)	C_a	-1.13380	0	0	0	-152.74949	0.91771	0.85252	-15.95955	-15.76868	129.84	50.16	60.70	0.72040	0.54620
$H_2C_a=C_b(H)(H)C=CR$ (1,3-butadiene, 1,3-pentadiene) $-HC_b=C_c(H)(H)C_c=C_bH-$ (1,3-cyclopentadiene)	C_b C_c	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	127.13	52.87	57.73	0.78613	0.48047
$H_2C_a=C_b(H)(H)C_b=C_c(H)C_dH_3$ (1,3-pentadiene) $H_2C_a=C_b(H)C_cH_2C_b(H)=C_aH_2$ (1,4-pentadiene) $-HC_b=C_c(H)(H)C_c=C_bH-$ (1,3-cyclopentadiene) $-H_2C_bC_c(H)=(H)C_cC_bH_2-$ (cyclopentene)	C_c C_b C_b C_c	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	127.61	52.39	58.24	0.77492	0.49168
$RC=C_{b,c}(H)-(H)C_{b,c}=CR'$ $(C-C$ (a))	$C_{b,c}$	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	78.31	101.69	36.16	1.54418	0.16123
$H_2C_a=C_b(H)(H)C_b=C_c(H)-C_dH_3$ (1,3-pentadiene) $-H_2C_b-C_c(H)=(H)C_c-C_bH_2-$ (cyclopentene) $(C-C$ (b))	C_c C_c	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	64.57	115.43	29.79	1.77684	0.34596
$H_2C_a=C_b(H)(H)C_b=C_c(H)-C_dH_3$ (1,3-pentadiene) $(C-C$ (b))	C_d	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	72.27	107.73	34.17	1.69388	0.26301
$-H_2C_b-C_c(H)=(H)C_c-C_bH_2-$ (cyclopentene) $(C-C$ (b))	C_b	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	65.99	114.01	30.58	1.76270	0.33183
$H_2C_a=C_b(H)-C_cH_2C_b(H)=C_aH_2$ (1,4-pentadiene) $(C-C$ (c)) $-H_2C_a-HC_b=C_c(H)(H)C_c=C_bH-$ (1,3-cyclopentadiene) $(C-C$ (d))	C_b C_b	-1.13380	-0.92918	0	0	-153.67866	0.91771	0.80561	-16.88873	-16.69786	64.57	115.43	29.79	1.77684	0.34596
$H_2C_a=C_b(H)-C_cH_2C_b(H)=C_aH_2$ (1,4-pentadiene) $(C-C$ (c)) $-H_2C_a-HC_b=C_c(H)(H)C_c=C_bH-$ (1,3-cyclopentadiene) $(C-C$ (d))	C_c C_a	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	65.99	114.01	30.58	1.76270	0.33183
$-H_2C_a-H_2C_bC_c(H)=(H)C_cC_bH_2-$ (cyclopentene) $(C-C$ (e))	C_a, C_b	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	56.41	123.59	26.06	1.90890	0.45116
$C-H$ (CH_2) (i)	C	-1.13380	0	0	0	-152.74949	0.91771	0.85252	-15.95955	-15.76868	77.15	102.85	41.13	1.23531	0.18965
$C-H$ (CH_3)	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H$ (CH_2) (ii)	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H$ (CH)	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326

Table 15.210. The energy parameters (eV) of functional groups of cyclic and conjugated alkenes.

Parameters	$C=C$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	CH_2 (i) Group	CH_3 Group	CH_2 (ii) Group	$C-H$ Group
n_1	2	1	1	1	1	1	2	3	2	1
n_2	0	0	0	0	0	0	1	2	1	0
n_3	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.75
C_2	0.91771	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1
c_2	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	0	0	1	0	1	0	1	1
c_4	4	2	2	2	2	2	1	1	1	1
c_5	0	0	0	0	0	0	2	3	2	1
C_{1o}	0.5	0.5	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.75
C_{2o}	0.91771	1	1	1	1	1	1	1	1	1
V_e (eV)	-102.08992	-33.01226	-30.19634	-30.19634	-30.19634	-28.79214	-72.03287	-107.32728	-70.41425	-35.12015
V_p (eV)	21.48386	9.83824	9.50874	9.50874	9.50874	9.33352	26.02344	38.92728	25.78002	12.87680
T (eV)	34.67062	8.63041	7.37432	7.37432	7.37432	6.77464	21.95990	32.53914	21.06675	10.48582
V_m (eV)	-17.33531	-4.31520	-3.68716	-3.68716	-3.68716	-3.38732	-10.97995	-16.26957	-10.53337	-5.24291
$E(_{AO/HO})$ (eV)	0	-14.63489	-14.63489	-14.63489	-14.63489	-15.56407	-14.63489	-15.56407	-15.56407	-14.63489
$\Delta E_{H_2MO}(_{AO/HO})$ (eV)	0	-1.85836	0	0	0	0	0	0	0	0
$E_T(_{AO/HO})$ (eV)	0	-12.77653	-14.63489	-14.63489	-14.63489	-15.56407	-14.63489	-15.56407	-15.56407	-14.63489
$E_T(_{H_2MO})$ (eV)	-63.27075	-31.63535	-31.63534	-31.63534	-31.63534	-31.63537	-49.66437	-67.69451	-49.66493	-31.63533
$E_T(atom-atom,msp^3.AO)$ (eV)	-2.26759	-2.26759	-1.85836	-1.85836	-1.85836	-1.85836	0	0	0	0
$E_T(_{MO})$ (eV)	-65.53833	-33.90295	-33.49373	-33.49373	-33.49373	-33.49373	-49.66493	-67.69450	-49.66493	-31.63537
ω $(10^{15}\ rad/s)$	43.0680	11.0522	9.97851	23.3291	9.97851	9.43699	25.2077	24.9286	24.2751	24.1759
E_K (eV)	28.34813	7.27475	6.56803	15.35563	6.56803	6.21159	16.59214	16.40846	15.97831	15.91299
$\bar{E}_D$ (eV)	-0.34517	-0.18090	-0.16982	-0.25966	-0.16982	-0.16515	-0.25493	-0.25352	-0.25017	-0.24966
$\bar{E}_{Kvib}$ (eV)	0.17897 [6]	0.14829 [48]	0.11159 [12]	0.11159 [12]	0.11159 [12]	0.12312 [2]	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)
$\bar{E}_{osc}$ (eV)	-0.25568	-0.10676	-0.11402	-0.20386	-0.11402	-0.10359	-0.07727	-0.22757	-0.14502	-0.07200
E_{mag} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(_{Group})$ (eV)	-66.04969	-34.00972	-33.60776	-33.69760	-33.60776	-33.59732	-49.81948	-67.92207	-49.80996	-31.70737
$E_{initial}(_{c_4\ AO/HO})$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(_{c_5\ AO/HO})$ (eV)	0	0	0	0	0	0	-13.59844	-13.59844	-13.59844	-13.59844
$E_D(_{Group})$ (eV)	7.51014	4.73994	4.33798	4.42782	4.18995	4.32754	7.83968	12.49186	7.83016	3.32601

Table 15.211. The total bond energies of cyclic and conjugated alkenes calculated using the functional group composition and the energies of Table 15.210 compared to the experimental values [2]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(_{Group})$ (eV) values based on composition is given by (15.58).

Formula	Name	$C=C$	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	CH_2 (i)	CH_3	CH_2 (ii)	CH	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_4H_6	1,3 Butadiene	2	1	0	0	0	0	2	0	0	2	0	42.09159	42.12705	0.00084
C_5H_8	1,3 Pentadiene	2	1	1	0	0	0	1	1	0	0	0	54.40776	54.42484	0.00031
C_5H_8	1,4 Pentadiene	2	0	0	2	0	0	2	0	1	2	0	54.03745	54.11806	0.00149
C_5H_6	1,3 Cyclopentadiene	2	1	0	0	2	0	0	0	1	4	0	49.27432	49.30294	0.00058
C_5H_8	Cyclopentene	1	0	2	0	0	2	0	0	3	2	-1	54.83565	54.86117	0.00047

Table 15.212. The bond angle parameters of cyclic and conjugated alkenes and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HC_aH$ $H_2C_a=C_b$ 1,3-butadiene	2.09132	2.09132	3.4928	-15.95955	9	H	H	0.85252	1	1	1	0.75	1.17300	0				113.25	
$\angle C_bC_aH_a$ $H_2C_a=C_b$ 1,3-butadiene																113.25		123.38	120.9 (1,3-butadiene)
$\angle C_bC_aH_a$ $H_2C_a=C_b$ 1,3-butadiene	2.53321	2.09132	4.0000	-15.95954 C_a	9	-15.95954 C_b	9	0.85252	0.85252	0.75	1	0.75	1.00000	0				119.45	120.9 (1,3-butadiene)
$\angle C_aC_bC_b$ $C_a=C_bC_b$ 1,3-butadiene	2.53321	2.76590	4.6904	-16.88873 C_a	27	-17.09334 C_b	30	0.80561	0.79597	1	1	1	0.85395	-1.85836				124.48	124.4 (1,3-butadiene CCC) 124.4 (1,3,5-hexatriene CbCcCc) 121.7 (1,3,5-hexatriene CaCbCc) 125.3 (2-butene CbCaCc)
$\angle C_bC_cC_c$ $C_b=C_cC_c$ 1,3-cyclopentadiene	2.53321	2.76590	4.3012	-17.81791 C_b	46	-17.81791 C_c	46	0.76360	0.76360	1	1	1	0.76360	-1.85836				108.44	109.4 (1,3-cyclopentadiene)
$\angle C_aC_bC_c$ $C_aC_b=C_c$ 1,3-cyclopentadiene	2.86175	2.53321	4.3818	-17.61330 C_a	42	-17.61330 C_c	42	0.77247	0.77247	1	1	1	0.77247	-1.85836				108.47	109.3 (1,3-cyclopentadiene)
$\angle C_bC_aC_b$ $=C_bHC_aH_2C_b(H)=$ 1,3-cyclopentadiene	2.86175	2.86175	4.4609	-17.40869 C_b	38	-17.40869 C_b	38	0.78155	0.78155	1	1	1	0.78155	-1.85836				102.41	102.8 (1,3-cyclopentadiene)
$\angle C_bC_cC_c$ $-H_2C_bHC_c=C_cHC_bH_2-$ cyclopentene	2.86175	2.53321	4.4272	-17.40869 C_b	38	-17.61330 C_b	42	0.78155	0.77247	1	1	1	0.77701	-1.85836				110.14	110.0 (cyclopentene)
$\angle C_aC_bC_c$ $-H_2C_aH_2C_bHC_c=C_cH-$ cyclopentene	2.91548	2.86175	4.5166	-17.20408 C_a	35	-17.40869 C_c	38	0.79085	0.78155	1	1	1	0.78620	-1.85836				102.85	103.0 (cyclopentene)
$\angle C_bC_aC_b$ $-C_bH_2C_aH_2C_bH_2-$ cyclopentene	2.91548	2.91548	4.5826	-17.20408 C_b	35	-17.20408 C_b	35	0.79085	0.79085	1	1	1	0.79085	-1.85836				103.61	104.0 (cyclopentene)

AROMATIC AND HETEROCYCLIC COMPOUNDS

Aromatic and heterocyclic molecules comprise at least one of an aromatic or a cyclic conjugated alkene functional group. The latter was described in the Cyclic and Conjugated Alkenes section. The aromatic bond is uniquely stable and requires the sharing of the electrons of multiple H_2-type MOs. The results of the derivation of the parameters of the benzene molecule given in the Benzene Molecule (C_6H_6) section can be generalized to any aromatic function group(s) of aromatic and heterocyclic compounds.

C_6H_6 can be considered a linear combination of three ethylene molecules wherein a $C-H$ bond of each CH_2 group of $H_2C=CH_2$ is replaced by a $C=C$ bond to form a six-member ring of carbon atoms. The solution of the ethylene molecule is given in the Ethylene Molecule (CH_2CH_2) section. The radius $r_{ethylene2sp^3}$ ($0.85252a_0$) of the $C2sp^3$ shell of ethylene calculated from the Coulombic energy is given by Eq. (14.244). The Coulombic energy $E_{Coulomb}\left(C_{ethylene},2sp^3\right)$ ($-15.95955\ eV$) of the outer electron of the $C2sp^3$ shell is given by Eq. (14.245). The energy $E\left(C_{ethylene},2sp^3\right)$ ($-15.76868\ eV$) of the outer electron of the $C2sp^3$ shell is given by Eq. (14.246). $E_T\left(C=C,2sp^3\right)$ ($-1.13380\ eV$) (Eq. (14.247), the energy change of each $C2sp^3$ shell with the formation of the $C=C$-bond MO is given by the difference between $E\left(C_{ethylene},2sp^3\right)$ and $E\left(C,2sp^3\right)$. C_6H_6 can be solved using the same principles as those used to solve ethylene wherein the $2s$ and $2p$ shells of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. Each $2sp^3$ HO of each carbon atom initially has four unpaired electrons. Thus, the $6H$ atomic orbitals (AOs) of benzene contribute six electrons and the six sp^3-hybridized carbon atoms contribute twenty-four electrons to form six $C-H$ bonds and six $C=C$ bonds. Each $C-H$ bond has two paired electrons with one donated from the H AO and the other from the $C2sp^3$ HO. Each $C=C$ bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from two sets of two $C2sp^3$ HOs of the participating carbon atoms. Each $C-H$ and each $C=C$ bond comprises a linear combination

of one and two diatomic H_2-type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section, respectively.

Consider the case where three sets of $C=C$-bond MOs form bonds between the two carbon atoms of each molecule to form a six-member ring such that the six resulting bonds comprise eighteen paired electrons. Each bond comprises a linear combination of two MOs wherein each comprises two $C2sp^3$ HOs and 75% of a H_2-type ellipsoidal MO divided between the $C2sp^3$ HOs:

$$\left(\begin{array}{l} 3\left(2\ C2sp^3 + 0.75\ H_2\ MO\right) \rightarrow 3\left(C\overset{4e}{=}C\right) - ethylene - type - bond\ MO \\ \rightarrow 6\left(C\overset{3e}{=}C\right) - bond\ MO\ of\ benzene \end{array} \right) \tag{15.142}$$

The linear combination of each H_2-type ellipsoidal MO with each $C2sp^3$ HO further comprises an excess 25% charge-density contribution per bond from each $C2sp^3$ HO to the $C=C$-bond MO to achieve an energy minimum. Thus, the dimensional parameters of each bond $C=C$-bond are determined using Eqs. (15.42) and (15.1-15.5) in a form that are the same equations as those used to determine the same parameters of the $C=C$-bond MO of ethylene (Eqs. (14.242-14.268)) while matching the boundary conditions of the structure of benzene.

Hybridization with 25% electron donation to each $C=C$-bond gives rise to the $C_{benzene}2sp^3$ HO-shell Coulombic energy $E_{Coulomb}\left(C_{benzene}, 2sp^3\right)$ given by Eq. (14.245). To meet the equipotential condition of the union of the six $C2sp^3$ HOs, c_2 and C_2 of Eq. (15.42) for the aromatic $C\overset{3e}{=}C$-bond MO is given by Eq. (15.62) as the ratio of 15.95955 eV, the magnitude of $E_{Coulomb}\left(C_{benzene}, 2sp^3\right)$ (Eq. (14.245)), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H (Eq. (1.243)):

$$C_2\left(benzeneC2sp^3HO\right) = c_2\left(benzeneC2sp^3HO\right) = \frac{13.605804\ eV}{15.95955\ eV} = 0.85252 \tag{15.143}$$

The energies of each $C\overset{3e}{=}C$ bond of benzene are also determined using the same equations as those of ethylene (Eqs. (14.251-14.253) and (14.319-14.333) with the parameters of benzene. Ethylene serves as a basis element for the $C\overset{3e}{=}C$ bonding of benzene wherein each of the six $C\overset{3e}{=}C$ bonds of benzene comprises $(0.75)(4) = 3$ electrons according to Eq. (15.142).

The total energy of the bonds of the eighteen electrons of the $C\overset{3e}{=}C$ bonds of benzene, $E_T\left(C_6H_6, C\overset{3e}{=}C\right)$, is given by $(6)(0.75)$ times $E_{T+osc}(C=C)$ (Eq. (14.492)), the total energy of the $C\overset{3e}{=}C$-bond MO of benzene including the Doppler term, minus eighteen times $E(C,2sp^3)$ (Eq. (14.146)), the initial energy of each $C2sp^3$ HO of each C that forms the $C\overset{3e}{=}C$ bonds of bond order two. Thus, the total energy of the six $C\overset{3e}{=}C$ bonds of benzene with three electron per aromatic bond given by Eq. (14.493) is

$$\begin{aligned} E_T\left(C_6H_6, C\overset{3e}{=}C\right) &= (6)(0.75)E_{T+osc}(C=C) - (6)(3)E(C,2sp^3) \\ &= (6)(0.75)(-66.05796\ eV) - 18(-14.63489\ eV) \\ &= -297.26081\ eV - (-263.42798\ eV) \\ &= -33.83284\ eV \end{aligned} \tag{15.144}$$

The results of benzene can be generalized to the class of aromatic and heterocyclic compounds. $E_{h\nu}$ of an aromatic bond is given by $E_T(H_2)$ (Eqs. (11.212) and (14.486)), the maximum total energy of each H_2-type MO such that

$$\overline{E}_{osc} = n_1\left(\overline{E}_D + \overline{E}_{Kvib}\right) = n_1\left(-31.63536831\ eV\sqrt{\frac{2\overline{E}_K}{Mc^2}} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \tag{15.145}$$

The factor of 0.75 corresponding to the three electrons per aromatic bond of bond order two given in the Benzene Molecule (C_6H_6) section modifies Eqs. (15.52-15.56). Multiplication of the total energy given by Eq. (15.55) by $f_1 = 0.75$ with the substitution of Eq. (15.145) gives the total energy of the aromatic bond:

$$E_T(Group) = f_1\left(\begin{array}{l} E(basis\ energies) + E_T(atom-atom, msp^3.AO) \\ -31.63536831\ eV\sqrt{\dfrac{2\hbar\sqrt{\dfrac{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o R^3}}{m_e}}}{m_ec^2}} + n_1\overline{E}_{Kvib} + c_3\dfrac{8\pi\mu_o\mu_B^2}{r^3} \end{array}\right) \tag{15.146}$$

The total bond energy of the aromatic group $E_D(Group)$ is the negative difference of the total energy of the group (Eq. (15.146)) and the total energy of the starting species given by the sum of $c_4 E_{initial}(c_4\ AO/HO)$ and $c_5 E_{initial}(c_5\ AO/HO)$:

$$E_D(Group) = -\left(f_1 \left(\begin{array}{l} E(basis\ energies) + E_T(atom-atom, msp^3.AO) \\ -31.63536831\ eV \sqrt{\dfrac{2\hbar\sqrt{\dfrac{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o R^3}}{m_e}}}{m_e c^2}} + n_1\bar{E}_{Kvib} + c_3 \dfrac{8\pi\mu_o\mu_B^2}{r^3} \end{array} \right) \\ -\left(c_4 E_{initial}(AO/HO) + c_5 E_{initial}(c_5\ AO/HO)\right) \right) \quad (15.147)$$

Since there are three electrons per aromatic bond, c_4 is three times the number of aromatic bonds.

Benzene can also be considered as comprising chemical bonds between six CH radicals wherein each radical comprises a chemical bond between carbon and hydrogen atoms. The solution of the parameters of CH is given in the Hydrogen Carbide (CH) section. Those of the benzene are given in the Benzene Molecule (C_6H_6) section. The energy components of V_e, V_p, T, V_m, and E_T are the same as those of the hydrogen carbide radical, except that $E_T(C=C,2sp^3) = -1.13379\ eV$ (Eq. (14.247)) is subtracted from $E_T(CH)$ of Eq. (13.495) to match the energy of each $C-H$-bond MO to the decrease in the energy of the corresponding $C2sp^3$ HO. In the corresponding generalization of the aromatic CH group, the geometrical parameters are determined using Eq. (15.42) and Eqs. (15.1-15.5) with $E_T(atom-atom, msp^3.AO) = -1.13379\ eV$.

The total energy of the benzene $C-H$-bond MO, $E_{T_{benzene}}(C-H)$, given by Eq. (14.467) is the sum of $0.5E_T(C=C,2sp^3)$, the energy change of each $C2sp^3$ shell per single bond due to the decrease in radius with the formation of the corresponding $\overset{3e}{C=C}$-bond MO (Eq. (14.247)), and $E_{T_{benzene}}(CH)$, the σ MO contribution given by Eq. (14.441). In the corresponding generalization of the aromatic CH group, the energy parameters are determined using Eqs. (15.146-15.147) with $f_1 = 1$ and $E_T(atom-atom, msp^3.AO) = \dfrac{-1.13379\ eV}{2}$. Thus, the energy

contribution to the single aromatic CH bond is one half that of the $C\overset{3e}{=}C$ double bond contribution. This matches the energies of the CH and $C\overset{3e}{=}C$ aromatic groups, conserves the electron number with the equivalent charge density as that of $s=1$ in Eqs. (15.18-15.21), and further gives a minimum energy for the molecule. Breakage of the aromatic $C\overset{3e}{=}C$ bonds to give CH groups creates unpaired electrons in these fragments that corresponds to $c_3=1$ in Eq. (15.56) with E_{mag} given by Eq. (15.58).

Each of the $C-H$ bonds of benzene comprises two electrons according to Eq. (14.439). From the energy of each $C-H$ bond, $-E_{D_{benzene}}\left({}^{12}CH\right)$ (Eq. (14.477)), the total energy of the twelve electrons of the six $C-H$ bonds of benzene, $E_T\left(C_6H_6,C-H\right)$, given by Eq. (14.494) is

$$E_T\left(C_6H_6,C-H\right)=\left(6\right)\left(-E_{D_{benzene}}\left({}^{12}CH\right)\right)=6\left(-3.90454\ eV\right)=-23.42724\ eV \tag{15.148}$$

The total bond dissociation energy of benzene, $E_D\left(C_6H_6\right)$, given by Eq. (14.495) is the negative sum of $E_T\left(C_6H_6,C\overset{3e}{=}C\right)$ (Eq. (14.493)) and $E_T\left(C_6H_6,C-H\right)$ (Eq. (14.494)):

$$\begin{aligned}E_D\left(C_6H_6\right)&=-\left(E_T\left(C_6H_6,C\overset{3e}{=}C\right)+E_T\left(C_6H_6,C-H\right)\right)\\&=-\left(\left(-33.83284\ eV\right)+\left(-23.42724\ eV\right)\right)\\&=57.2601\ eV\end{aligned} \tag{15.149}$$

Using the parameters given in Tables 15.214 and 15.216 in the general equations (Eqs. (15.42), (15.1-15.5), and (15.146-15.147)) reproduces the results for benzene given in the Benzene Molecule (C_6H_6) section as shown in Tables 15.214 and 15.216.

The symbols of the functional groups of aromatics and hertocyclics are given in Table 15.213. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of aromatics and hertocyclics are given in Tables 15.214, 15.215, and 15.216, respectively. The total energy of benzene given in Table 15.217 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.216 corresponding to functional-group composition of the molecule. The bond angle parameters of benzene determined using Eqs. (15.79-15.108) are given in Table 15.218.

Table 15.213. The symbols of functional groups of aromatics and hertocyclics.

Functional Group	Group Symbol
CC (aromatic bond)	$\overset{3e}{C=C}$
CH (aromatic)	CH (i)

Table 15.214. The geometrical bond parameters of aromatics and hertocyclics and experimental values [1].

Parameter	$\overset{3e}{C=C}$ Group	CH Group
a (a_0)	1.47348	1.60061
c' (a_0)	1.31468	1.03299
Bond Length $2c'$ $(\AA)$	1.39140	1.09327
Exp. Bond Length $(\AA)$	1.399 (benzene)	1.101 (benzene)
b,c (a_0)	0.66540	1.22265
e	0.89223	0.64537

Table 15.215. The MO to HO intercept geometrical bond parameters of benzene. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C-H$ (CH)	C	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$\overset{3e}{C=}HC_a\overset{3e}{=}C$	C_a	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533

Table 15.216. The energy parameters (eV) of functional groups of aromatics and hertocyclics.

Parameters	$\overset{3e}{C=C}$ Group	CH Group
f_1	0.75	1
n_1	2	1
n_2	0	0
n_3	0	0
C_1	0.5	0.75
C_2	0.85252	1
c_1	1	1
c_2	0.85252	0.91771
c_3	0	1
c_4	3	1
c_5	0	1
C_{1o}	0.5	0.75
C_{2o}	0.85252	1
$V_e\ (eV)$	-101.12679	-37.10024
$V_p\ (eV)$	20.69825	13.17125
$T\ (eV)$	34.31559	11.58941
$V_m\ (eV)$	-17.15779	-5.79470
$E(AO/HO)\ (eV)$	0	-14.63489
$\Delta E_{H_2MO}(AO/HO)\ (eV)$	0	-1.13379
$E_T(AO/HO)\ (eV)$	0	-13.50110
$E_T(H_2MO)\ (eV)$	-63.27075	-31.63539
$E_T(atom-atom, msp^3.AO)\ (eV)$	-2.26759	-0.56690
$E_T(MO)\ (eV)$	-65.53833	-32.20226
$\omega\ (10^{15}\ rad/s)$	49.7272	26.4826
$E_K\ (eV)$	32.73133	17.43132
$\bar{E}_D\ (eV)$	-0.35806	-0.26130
$\bar{E}_{Kvib}\ (eV)$	0.19649 [49]	0.35532 Eq. (13.458)
$\bar{E}_{osc}\ (eV)$	-0.25982	-0.08364
$E_{mag}\ (eV)$	0.14803	0.14803
$E_T(Group)\ (eV)$	-49.54347	-32.28590
$E_{initial}(c_4\ AO/HO)\ (eV)$	-14.63489	-14.63489
$E_{initial}(c_5\ AO/HO)\ (eV)$	0	-13.59844
$E_D(Group)\ (eV)$	5.63881	3.90454

Table 15.217. The total bond energies of benzene calculated using the functional group composition and the energies of Table 15.216 compared to the experimental values [2].

Formula	Name	$\overset{3e}{C=C}$	CH	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_6H_6	Benzene	6	6	57.26008	57.26340	0.00006

Table 15.218. The bond angle parameters of benzene and experimental values [1]. E_T is $E_T(atom-atom, msp^3.AO)$.

Atoms of Angle	2c' Bond 1 (a_0)	2c' Bond 2 (a_0)	2c' Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CCC$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	0.79232	-1.85836				120.19	120 [50-52] (benzene)
$\angle CCH$ (aromatic)																120.19		119.91	120 [50-52] (benzene)

NAPHTHALENE

Naphthalene has the formula $C_{10}H_8$ and comprises a planar molecule with two aromatic rings that share a common $C-C$ group. In order to be aromatic, the total number of bonding electrons must be a multiple of 3 since the number of electrons of the aromatic bond is $(0.75)(4)=3$ as shown in the Benzene section. In the case of naphthalene, the peripheral 10 carbons form the aromatic MO with the center bridged by a $C-C$ single bond. Then, 30 electrons of the 48 available form aromatic bonds, two electrons form the bridging $C-C$ single bond, and 16 electrons form the eight $C-H$ single bonds. The energies of the aromatic carbons are given by the same equations as those of benzene (Eqs. (15.42), (15.1-15.5), and (15.146-15.147)), except that there are 10 in naphthalene versus six in benzene. Since there are three electrons per aromatic bond, c_4 is three times ten, the number of aromatic bonds. Similarly, the aromatic $C-H$ group of naphthalene is equivalent to that of benzene.

To meet the equipotential condition of the union of the ten $C2sp^3$ HOs bridged by the $C-C$ single bond, the parameters c_1, C_2, and C_{2o} of Eq. (15.42) are one for the $C-C$ group, C_{1o} and C_1 are 0.5, and c_2 given by Eq. (15.142) is $c_2\left(C2sp^3HO\right)=0.85252$. Otherwise, the solutions of the $C-C$ bond parameters are equivalent to those of the replaced $C-H$ groups with $E(AO/HO)=-14.63489\ eV$ and $\Delta E_{H_2MO}(AO/HO)=-1.13379\ eV$ in Eq. (15.41). Similarly, the energy parameters are determined using Eqs. (15.52-15.56) with $E_T\left(atom-atom,msp^3.AO\right)=\dfrac{-1.13379\ eV}{2}$.

The symbols of the functional groups of naphthalene are given in Table 15.219. The corresponding designation of the structure is shown in Figure 62. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of naphthalene are given in Tables 15.220, 15.221, and 15.222, respectively. The total energy of naphthalene given in Table 15.223 was calculated as the sum over the integer multiple of each $E_D(_{Group})$ of Table 15.222 corresponding to functional-group composition of the molecule. The bond angle parameters of naphthalene determined using Eqs. (15.79-15.108) are given in Table 15.224.

Table 15.219. The symbols of functional groups of naphthalene.

Functional Group	Group Symbol
C_aC_a (aromatic bond)	$C\overset{3e}{=}C$
CH (aromatic)	CH (i)
C_b-C_b (bridging bond)	$C-C$

Table 15.220. The geometrical bond parameters of naphthalene and experimental values [1].

Parameter	$C\overset{3e}{=}C$ Group	CH Group	$C-C$ Group
a (a_0)	1.47348	1.60061	1.75607
c' (a_0)	1.31468	1.03299	1.32517
Bond Length $2c'$ $(Å)$	1.39140	1.09327	1.40250
Exp. Bond Length $(Å)$	1.40 (avg.) (naphthalene)	1.101 (benzene)	1.42 (naphthalene)
b,c (a_0)	0.66540	1.22265	1.15226
e	0.89223	0.64537	0.75462

Table 15.221. The MO to HO intercept geometrical bond parameters of naphthalene. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' $(°)$	θ_1 $(°)$	θ_2 $(°)$	d_1 (a_0)	d_2 (a_0)
$C-H$ (CH)	C	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$C\overset{3e}{=}HC_a\overset{3e}{=}C$	C_a	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533
$C\overset{3e}{=}C_a(C_b)\overset{3e}{=}C$	C_b	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	-16.61903	134.81	45.19	59.66	0.74430	0.57038
$(C_a)_2C_b-C_b(C_a)_2$	C_b	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	-16.61903	99.50	80.50	47.66	1.18269	0.14248

Table 15.222. The energy parameters (eV) of functional groups of naphthalene.

Parameters	$\overset{3e}{C=C}$ Group	CH Group	$C-C$ Group
f_1	0.75	1	1
n_1	2	1	1
n_2	0	0	0
n_3	0	0	0
C_1	0.5	0.75	0.5
C_2	0.85252	1	1
c_1	1	1	1
c_2	0.85252	0.91771	0.85252
c_3	0	1	0
c_4	3	1	2
c_5	0	1	0
C_{1o}	0.5	0.75	0.5
C_{2o}	0.85252	1	1
$V_e\ (eV)$	-101.12679	-37.10024	-34.43791
$V_p\ (eV)$	20.69825	13.17125	10.26723
$T\ (eV)$	34.31559	11.58941	9.80539
$V_m\ (eV)$	-17.15779	-5.79470	-4.90270
$E(AO/HO)\ (eV)$	0	-14.63489	-14.63489
$\Delta E_{H_2MO}(AO/HO)\ (eV)$	0	-1.13379	-1.13379
$E_T(AO/HO)\ (eV)$	0	-13.50110	-13.50110
$E_T(H_2MO)\ (eV)$	-63.27075	-31.63539	-31.63529
$E_T\left(atom-atom, msp^3.AO\right)\ (eV)$	-2.26759	-0.56690	-0.56690
$E_T(MO)\ (eV)$	-65.53833	-32.20226	-32.20226
$\omega\ \left(10^{15}\ rad/s\right)$	49.7272	26.4826	23.6343
$E_K\ (eV)$	32.73133	17.43132	15.55648
$\bar{E}_D\ (eV)$	-0.35806	-0.26130	-0.25127
$\bar{E}_{Kvib}\ (eV)$	0.19649 [49]	0.35532 Eq. (13.458)	0.12312 [2]
$\bar{E}_{osc}\ (eV)$	-0.25982	-0.08364	-0.18971
$E_{mag}\ (eV)$	0.14803	0.14803	0.14803
$E_T(Group)\ (eV)$	-49.54347	-32.28590	-32.39198
$E_{initial}(c_4\ AO/HO)\ (eV)$	-14.63489	-14.63489	-14.63489
$E_{initial}(c_5\ AO/HO)\ (eV)$	0	-13.59844	0
$E_D(Group)\ (eV)$	5.63881	3.90454	3.12220

Table 15.223. The total bond energies of naphthalene calculated using the functional group composition and the energies of Table 15.222 compared to the experimental values [2].

Formula	Name	$\overset{3e}{C=C}$	CH	$C-C$ Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_{10}H_8$	Naphthalene	10	8	1	90.74658	90.79143	0.00049

Table 15.224. The bond angle parameters of naphthalene and experimental values [1]. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle C_aC_cC_c$ (naphthalene)	2.62936	2.65034	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	0.79232	-1.85836				119.40	119.4 (naphthalene)
$\angle C_cC_aH$ (naphthalene)																119.40		120.30	
$\angle CCC$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	0.79232	-1.85836				120.19	120 [50-52] (benzene)
$\angle CCH$ (aromatic)																120.19		119.91	120 [50-52] (benzene)

TOLUENE

Toluene has the formula C_7H_8 and comprises the benzene molecule with one hydrogen atom replaced by a methyl group corresponding to a CH_3 functional group and a $C-C$ functional group. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The CH_3 functional group is the same as that of continuous and branched-chain alkanes given in the corresponding sections.

The bond between the methyl and aromatic ring comprises a $C-C$ functional group that is are solved using the same principles as those used to solve the alkane functional groups wherein the $2s$ and $2p$ AOs of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. To match energies within the MO that bridges methyl and aromatic carbons, $E(AO/HO)$ and $\Delta E_{H_2MO}(AO/HO)$ in Eq. (15.41) are $-15.35946\ eV$ (Eq. (14.155)) and $\frac{-1.13379\ eV}{2}$, respectively.

To meet the equipotential condition of the union of the aromatic and methyl $C2sp^3$ HOs of the $C-C$ single bond, the parameters c_1, C_2, and C_{2o} of Eq. (15.42) are one for the $C-C$ group, C_{1o} and C_1 are 0.5, and c_2 given by Eq. (13.430) is $c_2(C2sp^3HO)=0.91771$. To match the energies of the functional groups, $E_T(atom-atom,msp^3.AO)$ of the $C-C$-bond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is $-1.13379\ eV$ which is the same energy per $C2sp^3$ HO as that of the replaced $C-H$ group.

The symbols of the functional groups of toluene are given in Table 15.225. The corresponding designation of the structure is shown in Figure 63. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of toluene are given in Tables 15.226, 15.227, and 15.228, respectively. The total energy of toluene given in Table 15.229 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.228 corresponding to functional-group composition of the molecule. The bond angle parameters of toluene determined using Eqs. (15.79-15.108) are given in Table 15.230.

Table 15.225. The symbols of functional groups of toluene.

Functional Group	Group Symbol
CC (aromatic bond)	$\overset{3e}{C=C}$
CH (aromatic)	CH (i)
C_a-C_b (CH_3 to aromatic bond)	$C-C$
CH_3 group	$C-H$ (CH_3)

Table 15.226. The geometrical bond parameters of toluene and experimental values [1].

Parameter	$\overset{3e}{C=C}$ Group	CH (i) Group	$C-C$ Group	$C-H$ (CH_3) Group
a (a_0)	1.47348	1.60061	2.06004	1.64920
c' (a_0)	1.31468	1.03299	1.43528	1.04856
Bond Length $2c'$ $(Å)$	1.39140	1.09327	1.51904	1.10974
Exp. Bond Length $(Å)$	1.399 (toluene)	1.11 (avg.) (toluene)	1.524 (toluene)	1.11 (avg.) (toluene)
b,c (a_0)	0.66540	1.22265	1.47774	1.27295
e	0.89223	0.64537	0.69673	0.63580

Table 15.227. The MO to HO intercept geometrical bond parameters of toluene. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C-H$ (C_aH_3)	C_a	-0.56690	0	0	0	-152.18259	0.91771	0.88392	-15.39265	-15.20178	79.89	101.11	43.13	1.20367	0.15511
$C-H$ (C_cH)	C_c	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$\overset{3e}{C}=HC_c\overset{3e}{=}C$ $\overset{3e}{C}=(H_3C_a)C_b\overset{3e}{=}C$	C_c C_b	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533
$\left(\overset{3e}{C=}\right)_2 C_b-C_aH_3$	C_a	-0.56690	0	0	0	-152.18259	0.91771	0.88392	-15.39265	-15.20178	73.38	106.62	34.97	1.68807	0.25279
$\left(\overset{3e}{C=}\right)_2 C_b-C_aH_3$	C_b	-0.56690	-0.85035	-0.85035	0	-153.88328	0.91771	0.79597	-17.09334	-16.90247	61.56	118.44	28.27	1.81430	0.37901

Table 15.228. The energy parameters (eV) of functional groups of toluene.

Parameters	$\overset{3e}{C=C}$ Group	CH (i) Group	$C-C$ Group	CH_3 Group
f_1	0.75	1		
n_1	2	1	1	3
n_2	0	0	0	2
n_3	0	0	0	0
C_1	0.5	0.75	0.5	0.75
C_2	0.85252	1	1	1
c_1	1	1	1	1
c_2	0.85252	0.91771	0.91771	0.91771
c_3	0	1	0	0
c_4	3	1	2	1
c_5	0	1	0	3
C_{1o}	0.5	0.75	0.5	0.75
C_{2o}	0.85252	1	1	1
$V_e\ (eV)$	-101.12679	-37.10024	-29.95792	-107.32728
$V_p\ (eV)$	20.69825	13.17125	9.47952	38.92728
$T\ (eV)$	34.31559	11.58941	7.27120	32.53914
$V_m\ (eV)$	-17.15779	-5.79470	-3.63560	-16.26957
$E(AO/HO)\ (eV)$	0	-14.63489	-15.35946	-15.56407
$\Delta E_{H_2MO}(AO/HO)\ (eV)$	0	-1.13379	-0.56690	0
$E_T(AO/HO)\ (eV)$	0	-13.50110	-14.79257	-15.56407
$E_T(H_2MO)\ (eV)$	-63.27075	-31.63539	-31.63537	-67.69451
$E_T(atom-atom, msp^3.AO)\ (eV)$	-2.26759	-0.56690	-1.13379	0
$E_T(MO)\ (eV)$	-65.53833	-32.20226	-32.76916	-67.69450
$\omega\ (10^{15}\ rad/s)$	49.7272	26.4826	16.2731	24.9286
$E_K\ (eV)$	32.73133	17.43132	10.71127	16.40846
$\bar{E}_D\ (eV)$	-0.35806	-0.26130	-0.21217	-0.25352
$\bar{E}_{Kvib}\ (eV)$	0.19649 [49]	0.35532 Eq. (13.458)	0.14940 [53]	0.35532 (Eq. (13.458))
$\bar{E}_{osc}\ (eV)$	-0.25982	-0.08364	-0.13747	-0.22757
$E_{mag}\ (eV)$	0.14803	0.14803	0.14803	0.14803
$E_T(Group)\ (eV)$	-49.54347	-32.28590	-32.90663	-67.92207
$E_{initial}(c_4\ AO/HO)\ (eV)$	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(c_5\ AO/HO)\ (eV)$	0	-13.59844	0	-13.59844
$E_D(Group)\ (eV)$	5.63881	3.90454	3.63685	12.49186

Table 15.229. The total bond energies of toluene calculated using the functional group composition and the energies of Table 15.228 compared to the experimental values [2].

Formula	Name	$\overset{3e}{C=C}$	CH (i)	$C-C$ Group	CH_3	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_7H_8	Toluene	6	5	1	1	69.48425	69.546	0.00088

Table 15.230. The bond angle parameters of toluene and experimental values [1]. E_T is $E_T(atom-atom, msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CCC$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	0.79232	-1.85836				120.19	120 [50-52] (benzene)
$\angle CCH$ (aromatic)																120.19		119.91	120 [50-52] (benzene)

CHLOROBENZENES

Chlorobenzenes have the formula $C_6H_{6-m}Cl_m$ and comprise the benzene molecule with at least one hydrogen atom replaced by a chlorine atom corresponding to a $C-Cl$ functional group. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section.

The small differences between energies of ortho, meta, and para-dichlorobenzene is due to differences in the energies of vibration in the transition state that contribute to E_{osc}. Two types of $C-Cl$ functional groups can be identified based on symmetry that determine the parameter R in Eq. (15.48). One corresponds to the special case of 1,3,5 substitution and the other corresponds to other cases of single or multiple substitutions of Cl for H. P-dichlorobenzene is representative of the bonding with $R=a$. 1,2,3-trichlorbenzene is the particular case wherein is $R=b$. Also, beyond the binding of three chlorides E_{mag} is subtracted for each additional Cl due to the formation of an unpaired electrons on each $C-Cl$ bond.

The bond between the chlorine and aromatic ring comprises two $C-Cl$ functional groups that are solved using the same principles as those used to solve the alkyl chloride functional groups as given in the corresponding section wherein the $2s$ and $2p$ AOs of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and Cl AO to form a MO permits each participating hybridized orbital to decrease in radius and energy. As in the case of alkyl chlorides, c_2 of Eq. (15.52) for each $C-Cl$-bond MO is one, and the energy matching condition is determined by the C_2 parameter given by Eq. (15.111) which is $C_2(C2sp^3HO\ to\ Cl)=0.81317$. To match energies within the MO that bridges the chlorine AO and aromatic carbon $C2sp^3$ HO, $E(AO/HO)$ and $\Delta E_{H_2MO}(AO/HO)$ in Eq. (15.42) are $-14.63489\ eV$ and $-2.99216\ eV$, respectively. The latter matches twice that of the replaced $C-H$-bond MO plus $E_T(atom-atom,msp^3.AO)$. To match the energies of the functional groups, $E_T(atom-atom,msp^3.AO)$ of the $C-Cl$-bond MO in Eq. (15.53) due to the charge donation from the C and Cl atoms to the MO is $-0.72457\ eV$ (Eq. (14.151)).

The symbols of the functional groups of chlorobenzenes are given in Table 15.231. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of chlorobenzenes are given in Tables 15.232, 15.233, and 15.234, respectively. The total energy of each chlorobenzene given in Table 15.235 was calculated as the sum over the integer multiple of each $E_D(_{Group})$ of Table 15.234 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage , the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(_{Group})$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of chlorobenzenes determined using Eqs. (15.79-15.108) are given in Table 15.236.

Table 15.231. The symbols of functional groups of chlorobenzenes.

Functional Group	Group Symbol
CC (aromatic bond)	$C\overset{3e}{=}C$
CH (aromatic)	CH (i)
$Cl-C$ (Cl to aromatic bond)	$C-Cl$ (a)
$Cl-C$ (Cl to aromatic bond of 1,3,5-trichlorbenzene)	$C-Cl$ (b)

Table 15.232. The geometrical bond parameters of chlorobenzenes and experimental values [1].

Parameter	$C\overset{3e}{=}C$ Group	CH (i) Group	$C-Cl$ (a) Group	$C-Cl$ (b) Group
$a\ (a_0)$	1.47348	1.60061	2.20799	2.20799
$c'\ (a_0)$	1.31468	1.03299	1.64782	1.64782
Bond Length $2c'$ (Å)	1.39140	1.09327	1.74397	1.74397
Exp. Bond Length (Å)	1.400 (chlorobenzene)	1.083 (chlorobenzene)	1.737 (chlorobenzene)	1.737 (chlorobenzene)
$b,c\ (a_0)$	0.66540	1.22265	1.46967	1.46967
e	0.89223	0.64537	0.74630	0.74630

Table 15.233. The MO to HO intercept geometrical bond parameters of chlorobenzenes. E_T is $E_T(atom-atom, msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}\ (a_0)$	$r_{final}\ (a_0)$	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	$d_1\ (a_0)$	$d_2\ (a_0)$
$C-H\ (C_bH)$	C_b	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$C\overset{3e}{=}HC_b\overset{3e}{=}C$	C_b	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533
$\left(C\overset{3e}{=}\right)_2 C_a-Cl$	C_a	-0.36229	-0.85035	-0.85035	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	73.32	106.68	31.67	1.87911	0.23129
$\left(C\overset{3e}{=}\right)_2 C_a-Cl$	Cl	-0.36229	0	0	0		1.05158	0.89582	15.18804		82.92	97.08	37.22	1.75824	0.11042
$C_b\overset{3e}{=}(Cl)C_a\overset{3e}{=}C_b$ (C_b bound to H or Cl)	C_a	-0.36229	-0.85035	-0.85035	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	134.65	45.35	59.47	0.74854	0.56614

Table 15.23.1. The energy parameters (eV) of functional groups of chlorobenzenes.

Parameters	$C\overset{3e}{=}C$ Group	CH (i) Group	$C-Cl$ (a) Group	$C-Cl$ (b) Group
f_1	0.75	1		
n_1	2	1	1	1
n_2	0	0	0	0
n_3	0	0	0	0
C_1	0.5	0.75	0.5	0.5
C_2	0.85252	1	0.81317	0.81317
c_1	1	1	1	1
c_2	0.85252	0.91771	1	1
c_3	0	1	0	0
c_4	3	1	2	2
c_5	0	1	0	0
C_{1o}	0.5	0.75	0.5	0.5
C_{2o}	0.85252	1	0.81317	0.81317
V_e (eV)	-101.12679	-37.10024	-31.85648	-31.85648
V_p (eV)	20.69825	13.17125	8.25686	8.25686
T (eV)	34.31559	11.58941	7.21391	7.21391
V_m (eV)	-17.15779	-5.79470	-3.60695	-3.60695
$E(_{AO/HO})$ (eV)	0	-14.63489	-14.63489	-14.63489
$\Delta E_{H_2MO}(_{AO/HO})$ (eV)	0	-1.13379	-2.99216	-2.99216
$E_T(_{AO/HO})$ (eV)	0	-13.50110	-11.64273	-11.64273
$E_T(_{H_2MO})$ (eV)	-63.27075	-31.63539	-31.63539	-31.63539
$E_T\left(atom-atom, msp^3.AO\right)$ (eV)	-2.26759	-0.56690	-0.72457	-0.72457
$E_T(_{MO})$ (eV)	-65.53833	-32.20226	-32.35994	-32.35994
ω $\left(10^{15}\ rad/s\right)$	49.7272	26.4826	8.03459	14.7956
E_K (eV)	32.73133	17.43132	5.28851	9.73870
$\bar{E}_D$ (eV)	-0.35806	-0.26130	-0.14722	-0.19978
$\bar{E}_{Kvib}$ (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.08059 [12]	0.08059 [12]
$\bar{E}_{osc}$ (eV)	-0.25982	-0.08364	-0.10693	-0.15949
E_{mag} (eV)	0.14803	0.14803	0.14803	0.14803
$E_T(_{Group})$ (eV)	-49.54347	-32.28590	-32.46687	-32.51943
$E_{initial}(_{c_4\ AO/HO})$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(_{c_5\ AO/HO})$ (eV)	0	-13.59844	0	0
$E_D(_{Group})$ (eV)	5.63881	3.90454	3.19709	3.24965

Table 15.235. The total bond energies of chlorobenzenes calculated using the functional group composition and the energies of Table 15.234 compared to the experimental values [2]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_{D(group)}$ (eV) values based on composition is given by (15.58).

Formula	Name	$C\overset{3e}{=}C$	CH (i)	$C-Cl$ (a) Group	$C-Cl$ (b) Group	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_6H_5Cl	Chlorobenzene	6	5	1	0	0	56.55263	56.581	0.00051
$C_6H_4Cl_2$	m-dichlorobenzene	6	4	2	0	0	55.84518	55.852	0.00012
$C_6H_3Cl_3$	1,2,3-trichlorobenzene	6	3	3	0	0	55.13773	55.077	-0.00111
$C_6H_3Cl_3$	1,3,5-trichlorbenzene	6	3	0	1	0	55.29542	55.255	-0.00073
C_6Cl_6	Hexachlorobenzene	6	0	6	0	3	52.57130	52.477	-0.00179

Table 15.236. The bond angle parameters of chlorobenzenes and experimental values [1]. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CCC$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	0.79232	-1.85836				120.19	120 ($\angle CC(H)C$ chlorobenzene) 121.7 ($\angle CC(Cl)C$ chlorobenzene) 120 [50-52] (benzene)
$\angle CCH$ $\angle CCCl$ (aromatic)																120.19		119.91	120 [50-52] (benzene)

PHENOL

Phenol has the formula C_6H_6O and comprises the benzene molecule with one hydrogen atom replaced by a hydroxyl corresponding to an OH functional group and a $C-O$ functional group. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The OH functional group is the same as that of alcohols given in the corresponding section.

The bond between the hydroxyl and aromatic ring comprises a $C-O$ functional group that is are solved using the same principles as those used to solve the alcohol functional groups wherein the $2s$ and $2p$ AOs of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and O AO to form a MO permits each participating hybridized orbital to decrease in radius and energy. In aryl alcohols, the aromatic $C2sp^3$ HO has a hybridization factor of 0.85252 (Eq. (15.143)) with an initial energy of $E\left(C,2sp^3\right)=-14.63489\ eV$ (Eq. (15.25)) and the O AO has an energy of $E\left(O\right)=-13.61806\ eV$. To meet the equipotential condition of the union of the $C-O$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the $C-O$-bond MO given by Eqs. (15.68) and (15.70) is

$$\begin{aligned} c_2\left(arylC2sp^3HO\ to\ O\right) &= \frac{E(O)}{E\left(C,2sp^3\right)}c_2\left(arylC2sp^3HO\right) \\ &= \frac{-13.61806\ eV}{-14.63489\ eV}(0.85252) \\ &= 0.79329 \end{aligned} \tag{15.150}$$

$E_T\left(atom-atom,msp^3.AO\right)$ of the $C-O$-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is $-1.49608\ eV$. It is based on the energy match between the OH group and the $C2sp^3$ HO of an aryl group and is given by the linear combination of $-0.92918\ eV$ (Eq. (14.513)) and $-1.13379\ eV$ (Eq. (14.247)), respectively.

The symbols of the functional groups of phenol are given in Table 15.237. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of phenol are given in Tables 15.238, 15.239, and 15.240, respectively. The total energy of phenol given in Table 15.241 was calculated as the sum over the integer multiple of each $E_D(_{Group})$ of Table 15.240

corresponding to functional-group composition of the molecule. The bond angle parameters of phenol determined using Eqs. (15.79-15.108) are given in Table 15.242.

Table 15.237. The symbols of functional groups of phenol.

Functional Group	Group Symbol
CC (aromatic bond)	$C\overset{3e}{=}C$
CH (aromatic)	CH (i)
Aryl C-O	$C-O$ (a)
OH group	OH

Table 15.238. The geometrical bond parameters of phenol and experimental values [1].

Parameter	$C\overset{3e}{=}C$ Group	CH (i) Group	$C-O$ (a) Group	OH Group
$a\ (a_0)$	1.47348	1.60061	1.68220	1.26430
$c'\ (a_0)$	1.31468	1.03299	1.29700	0.91808
Bond Length $2c'\ (\mathring{A})$	1.39140	1.09327	1.37268	0.971651
Exp. Bond Length $(\mathring{A})$	1.397 avg. (phenol)	1.084 (phenol)	1.364 (phenol)	0.956 (phenol)
$b,c\ (a_0)$	0.66540	1.22265	1.07126	0.86925
e	0.89223	0.64537	0.77101	0.72615

Table 15.239. The MO to HO intercept geometrical bond parameters of phenol. E_T is $E_T(atom-atom, msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C-H\ (C_bH)$	C_b	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$\left(C_b \overset{3e}{=}\right)_2 C_aO-H$	O	-0.74804	0	0	0		1.00000	0.87363	-15.57379		115.79	64.21	64.82	0.53799	0.38009
$\left(C_b \overset{3e}{=}\right)_2 C_a-OH$	C_a	-0.74804	-0.85035	-0.85035	0	-154.06442	0.91771	0.78762	-17.27448	-17.08362	100.00	80.00	46.39	1.16026	0.13674
$\left(C_b \overset{3e}{=}\right)_2 C_a-OH$	O	-0.74804	0	0	0		1.00000	0.87363	15.57379		106.51	73.49	51.43	1.04871	0.24829
$\left(C_b \overset{3e}{=}\right)_2 C_aOH$	C_a	-0.74804	-0.85035	-0.85035	0	-154.06442	0.91771	0.78762	-17.27448	-17.08362	133.88	46.12	58.55	0.76870	0.54598
$\left(\overset{3e}{=}(H)C_b\right)_2 C_aOH$	C_b	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533

Table 15.240. The energy parameters (eV) of functional groups of phenol.

Parameters	$\overset{3e}{C=C}$ Group	CH (i) Group	$C-O$ (a) Group	OH Group
f_1	0.75	1		
n_1	2	1	1	1
n_2	0	0	0	0
n_3	0	0	0	0
C_1	0.5	0.75	0.5	0.75
C_2	0.85252	1	1	1
c_1	1	1	1	0.75
c_2	0.85252	0.91771	0.79329	1
c_3	0	1	0	1
c_4	3	1	2	1
c_5	0	1	0	1
C_{1o}	0.5	0.75	0.5	0.75
C_{2o}	0.85252	1	1	1
V_e (eV)	-101.12679	-37.10024	-34.04658	-40.92709
V_p (eV)	20.69825	13.17125	10.49024	14.81988
T (eV)	34.31559	11.58941	10.11966	16.18567
V_m (eV)	-17.15779	-5.79470	-5.05983	-8.09284
$E(_{AO/HO})$ (eV)	0	-14.63489	-14.63489	-13.6181
$\Delta E_{H_2MO}(_{AO/HO})$ (eV)	0	-1.13379	-1.49608	0
$E_T(_{AO/HO})$ (eV)	0	-13.50110	-13.13881	-13.6181
$E_T(_{H_2MO})$ (eV)	-63.27075	-31.63539	-31.63532	-31.63247
$E_T\left(atom-atom,msp^3.AO\right)$ (eV)	-2.26759	-0.56690	-1.49608	0
$E_T(_{MO})$ (eV)	-65.53833	-32.20226	-33.13145	-31.63537
ω $\left(10^{15}\ rad/s\right)$	49.7272	26.4826	13.3984	44.1776
E_K (eV)	32.73133	17.43132	8.81907	29.07844
$\bar{E}_D$ (eV)	-0.35806	-0.26130	-0.19465	-0.33749
$\bar{E}_{Kvib}$ (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.12808 [19]	0.46311 [17-18]
$\bar{E}_{osc}$ (eV)	-0.25982	-0.08364	-0.13061	-0.10594
E_{mag} (eV)	0.14803	0.14803	0.14803	0.11441
$E_T(_{Group})$ (eV)	-49.54347	-32.28590	-33.26206	-31.74130
$E_{initial}(_{c_4\ AO/HO})$ (eV)	-14.63489	-14.63489	-14.63489	-13.6181
$E_{initial}(_{c_5\ AO/HO})$ (eV)	0	-13.59844	0	-13.59844
$E_D(_{Group})$ (eV)	5.63881	3.90454	3.99228	4.41035

Table 15.241. The total bond energies of phenol calculated using the functional group composition and the energies of Table 15.240 compared to the experimental values [2].

Formula	Name	$\overset{3e}{C=C}$	CH (i)	$C-O$ (a) Group	OH Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_6H_6O	Phenol	6	5	1	1	61.75817	61.704	-0.00087

Table 15.242. The bond angle parameters of phenol and experimental values [1]. E_T is $E_T(atom-atom, msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CCC$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	0.79232	-1.85836				120.19	120 [50-52] (benzene)
$\angle CCH$ (aromatic)																120.19		119.91	120 [50-52] (benzene)
$\angle C_aOH$	2.59399	1.83616	3.6315	-14.82575	1	-14.82575	1	1	0.91771	0.75	1	0.75	0.91771	0				109.84	109.0 (phenol)

ANILNE

Aniline and methyl aniline have the formula C_6H_7N and C_7H_9N, respectively. They comprise the benzene and toluene molecules with one hydrogen atom replaced by an amino group corresponding to an NH_2 functional group and a $C-N$ functional group. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The $C-C$ and CH_3 functional groups of methyl anilines are equivalent to those of toluene given in the corresponding section.

The aryl amino (NH_2) functional group was solved using the procedure given in the Dihydrogen Nitride (NH_2) section. Using the results of Eqs. (13.245-13.368), the aryl amino parameters in Eq. (15.51) are $n_1 = 2$, $C_1 = 0.75$, $C_2 = 0.93613$ (Eqs. (13.248-13.249)), $C_{1o} = 1.5$, and $c_1 = 0.75$. In the determination of the hybridization factor c_2 of Eq. (15.52) for the $N-H$-bond MO of aryl amines, the $C2sp^3$ HO of the $C-NH_2$-bond MO has an energy of $E(C,2sp^3) = -15.76868\ eV$ (Eq. (15.18) corresponding to $s=2$ in Eqs. (15.18-15.20), and the N AO has an energy of $E(N) = -14.53414\ eV$. To meet the equipotential condition of the union of the $N-H$ H_2-type-ellipsoidal-MO with the $C2sp^3$ HO, the hybridization factor c_2 given by Eq. (15.68) is

$$c_2(H\ to\ \text{anline}\ N) = \frac{E(N)}{E(C,2sp^3)} = \frac{-14.53414\ eV}{-15.76868\ eV} = 0.92171 \tag{15.151}$$

The bond between the amino and aromatic ring comprises a $C-N$ functional group that is the same as that of 2° amines (methylene) except that the energies corresponding to oscillation in the transition state are those of aniline. The group is solved using the same principles as those used to solve the primary and secondary-amine functional groups wherein the $2s$ and $2p$ AOs of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and N AO to form a MO permits each participating hybridized orbital to decrease in radius and energy. The hybridization is determined in a similar manner to that of the $C-O$ group of phenol. In anilines, the aromatic $C2sp^3$ HO has a hybridization factor of 0.85252 (Eq. (15.143)) with an initial energy of $E(C,2sp^3) = -14.63489\ eV$ (Eq. (15.25)) and the N AO has an energy

of $E(N) = -14.53414\ eV$. To meet the equipotential condition of the union of the $C-O$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.51) for the $C-O$-bond MO given by Eqs. (15.68) and (15.70) is

$$\begin{aligned} c_2(arylC2sp^3HO\ to\ N) &= \frac{E(N)}{E(C,2sp^3)} c_2(arylC2sp^3HO) \\ &= \frac{-14.53414\ eV}{-14.63489\ eV}(0.85252) \\ &= 0.84665 \end{aligned} \tag{15.152}$$

$E_T(atom-atom,msp^3.AO)$ of the $C-N$-bond MO in Eq. (15.52) due to the charge donation from the C and N atoms to the MO is $-1.13379\ eV$ (Eq. (14.247)). It is based on the energy match between the NH_2 group and the $C2sp^3$ HO of the aryl group and is twice that of the aryl $C-H$ group that it replaces.

The symbols of the functional groups of aniline and methyl-substituted anilines are given in Table 15.243. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of aniline and methyl-substituted anilines are given in Tables 15.244, 15.245, and 15.246, respectively. The total energy of each aniline and methyl-substituted aniline given in Table 15.247 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.246 corresponding to functional-group composition of the molecule. The bond angle parameters of aniline and methyl-substituted anilines determined using Eqs. (15.79-15.108) are given in Table 15.248.

Table 15.243. The symbols of functional groups of aniline and methyl-substituted anilines.

Functional Group	Group Symbol
CC (aromatic bond)	$C\overset{3e}{=}C$
CH (aromatic)	CH (i)
Aryl C-N	$C-N$ (a)
NH_2 group	NH_2
C_a-C_b (CH_3 to aromatic bond)	$C-C$ (a)
CH_3 group	$C-H$ (CH_3)

Table 15.244. The geometrical bond parameters of aniline and methyl-substituted anilines and experimental values [1].

Parameter	$\overset{3e}{C=C}$ Group	CH (i) Group	$C-N$ (a) Group	NH_2 Group	$C-C$ (a) Group	$C-H$ (CH_3) Group
a (a_0)	1.47348	1.60061	1.81158	1.24428	2.06004	1.64920
c' (a_0)	1.31468	1.03299	1.34595	0.94134	1.43528	1.04856
Bond Length $2c'$ $(Å)$	1.39140	1.09327	1.42449	0.99627	1.51904	1.10974
Exp. Bond Length $(Å)$	1.397 avg. (phenol)	1.084 (phenol)	1.431 (aniline)	0.998 (aniline)	1.524 (toluene)	1.11 (avg.) (toluene)
b,c (a_0)	0.66540	1.22265	1.21254	0.81370	1.47774	1.27295
e	0.89223	0.64537	0.74297	0.75653	0.69673	0.63580

Table 15.245. The MO to HO intercept geometrical bond parameters of aniline and methyl-substituted anilines. E_T is $E_T(atom-atom, msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' $(^\circ)$	θ_1 $(^\circ)$	θ_2 $(^\circ)$	d_1 (a_0)	d_2 (a_0)
$C-H$ (C_bH)	C_b	-0.85035	-0.85035	-0.56690	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$C-H$ (C_aH_3)	C_a	-0.56690	0	0	0	-152.18259	0.91771	0.88392	-15.39265	-15.20178	79.89	101.11	43.13	1.20367	0.15511
$\left(C_b\overset{3e}{=}\right)_2 C_aNH-H$	N	-0.56690	0	0	0		0.93084	0.88392	-15.39265		121.74	58.26	67.49	0.47634	0.46500
$\left(C_b\overset{3e}{=}\right)_2 C_a-NH_2$	C_a	-0.56690	-0.85035	-0.85035	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	88.49	91.51	41.01	1.36696	0.02101
$\left(C_b\overset{3e}{=}\right)_2 C_a-NH_2$	N	-0.56690	0	0	0		0.93084	0.88392	-15.39265		96.32	83.68	46.43	1.24859	0.09736
$\left(C\overset{3e}{=}\right)_2 C_b-C_aH_3$	C_a	-0.56690	0	0	0	-152.18259	0.91771	0.88392	-15.39265	-15.20178	73.38	106.62	34.97	1.68807	0.25279
$\left(C\overset{3e}{=}\right)_2 C_b-C_aH_3$	C_b	-0.56690	-0.85035	-0.85035	0	-153.88328	0.91771	0.79597	-17.09334	-16.90247	61.56	118.44	28.27	1.81430	0.37901
$C\overset{3e}{=}HC_c\overset{3e}{=}C$ $C\overset{3e}{=}(H_2N)C_a\overset{3e}{=}C$ $C\overset{3e}{=}(H_3C_a)C_b\overset{3e}{=}C$	C_c C_a C_b	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533

Table 15.246. The energy parameters (eV) of functional groups of aniline and methyl-substituted anilines.

Parameters	$\overset{3e}{C=C}$ Group	CH (i) Group	$C-N$ (a) Group	NH_2 Group	$C-C$ (a) Group	CH_3 Group
f_1	0.75	1				
n_1	2	1	1	2	1	3
n_2	0	0	0	0	0	2
n_3	0	0	0	1	0	0
C_1	0.5	0.75	0.5	0.75	0.5	0.75
C_2	0.85252	1	1	0.93613	1	1
c_1	1	1	1	0.75	1	1
c_2	0.85252	0.91771	0.84665	0.92171	0.91771	0.91771
c_3	0	1	0	0	0	0
c_4	3	1	2	1	2	1
c_5	0	1	0	2	0	3
C_{1o}	0.5	0.75	0.5	1.5	0.5	0.75
C_{2o}	0.85252	1	1	1	1	1
$V_e\ (eV)$	-101.12679	-37.10024	-32.76465	-78.97795	-29.95792	-107.32728
$V_p\ (eV)$	20.69825	13.17125	10.10870	28.90735	9.47952	38.92728
$T\ (eV)$	34.31559	11.58941	9.04312	31.73641	7.27120	32.53914
$V_m\ (eV)$	-17.15779	-5.79470	-4.52156	-15.86820	-3.63560	-16.26957
$E(AO/HO)\ (eV)$	0	-14.63489	-14.63489	-14.53414	-15.35946	-15.56407
$\Delta E_{H_2MO}(AO/HO)\ (eV)$	0	-1.13379	-1.13379	0	-0.56690	0
$E_T(AO/HO)\ (eV)$	0	-13.50110	-13.50110	-14.53414	-14.79257	-15.56407
$E(n_3\ AO/HO)\ (eV)$	0	0	0	-14.53414	0	0
$E_T(H_2MO)\ (eV)$	-63.27075	-31.63539	-31.63549	-48.73654	-31.63537	-67.69451
$E_T\left(atom-atom,msp^3.AO\right)\ (eV)$	-2.26759	-0.56690	-1.13379	0	-1.13379	0
$E_T(MO)\ (eV)$	-65.53833	-32.20226	-32.76916	-48.73660	-32.76916	-67.69450
$\omega\ \left(10^{15}\ rad/s\right)$	49.7272	26.4826	11.9890	68.9812	16.2731	24.9286
$E_K\ (eV)$	32.73133	17.43132	7.89138	45.40465	10.71127	16.40846
$\bar{E}_D\ (eV)$	-0.35806	-0.26130	-0.18211	-0.42172	-0.21217	-0.25352
$\bar{E}_{Kvib}\ (eV)$	0.19649 [49]	0.35532 Eq. (13.458)	0.15498 [54]	0.40929 [22]	0.14940 [53]	0.35532 (Eq. (13.458))
$\bar{E}_{osc}\ (eV)$	-0.25982	-0.08364	-0.10462	-0.21708	-0.13747	-0.22757
$E_{mag}\ (eV)$	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(Group)\ (eV)$	-49.54347	-32.28590	-32.87379	-49.17075	-32.90663	-67.92207
$E_{initial}(c_4\ AO/HO)\ (eV)$	-14.63489	-14.63489	-14.63489	-14.53414	-14.63489	-14.63489
$E_{initial}(c_5\ AO/HO)\ (eV)$	0	-13.59844	0	-13.59844	0	-13.59844
$E_D(Group)\ (eV)$	5.63881	3.90454	3.60401	7.43973	3.63685	12.49186

Table 15.247. The total bond energies of aniline and methyl-substituted anilines calculated using the functional group composition and the energies of Table 15.246 compared to the experimental values [2].

Formula	Name	$\overset{3e}{C=C}$	CH (i)	$C-N$ (a) Group	NH_2 Group	$C-C$ (a) Group	CH_3	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_6H_7N	Aniline	6	5	1	1	0	0	64.43373	64.374	-0.00093
C_7H_9N	2-methylaniline	6	4	1	1	1	1	76.62345	76.643	-0.00025
C_7H_9N	3-methylaniline	6	4	1	1	1	1	76.62345	76.661	0.00050
C_7H_9N	4-methylaniline	6	4	1	1	1	1	76.62345	76.654	0.00040

Table 15.248. The bond angle parameters of aniline and methyl-substituted anilines and experimental values [1]. E_T is $E_T\left(atom-atom,msp^3.AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CCC$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	0.79232	-1.85836				120.19	120 [50-52] (benzene)
$\angle CCH$ (aromatic)																120.19		119.91	120 [50-52] (benzene)
$\angle HNH$	1.88268	1.88268	3.1559	-14.53414	N	H	H	0.93613 Eq. (13.248))	1	1	1	0.75	1.06823	0				113.89	113.9 (aniline)
$\angle HNC_a$	1.88268	2.69190	4.0332	-14.53414	N	-15.95955	9	0.84665 (Eq. (15.152))	0.86284 (Eq. (15.64))	0.75	1	0.75	1.01912	0				122.70	

ARYL NITRO COMPOUNDS

Aryl nitro compounds have a hydrogen of an aryl group replaced by a nitro corresponding to an NO_2 functional group and a $C-N$ functional group. Examples include nitrobenzene, nitrophenol, and nitroanilne with formulas $C_6H_5NO_2$, $C_6H_5NO_3$, and $C_6H_6N_2O_2$, respectively. The aromatic $C \overset{3e}{=} C$ and $C-H$ functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The OH and $C-O$ functional groups of nitrophenols are the same as those of phenol given in the corresponding section. The NH_2 and $C-N$ functional groups of nitroanilines are the same as those of aniline given in the corresponding section. The differences between the total bond energies of the nitroanilines given in Table 15.252 are due to differences in the E_{osc} term. For simplicity and since the differences are small, the E_{osc} terms for nitroanilines were taken as the same.

The NO_2 group is the same as that given in the Nitroalkanes section. The bond between the nitro and aromatic ring comprises a $C-N$ functional group that is the same as that of nitroalkanes given in the corresponding section except that $E_T\left(atom-atom, msp^3.AO\right)$ is $-0.72457\ eV$, one half of that of the $C-N$-bond MO of nitroalkanes and equivalent to that of methyl (Eq. (14.151)) in order to maintain the independence and aromaticity of the benzene functional group. In addition, the energy terms due to oscillation in the transition state correspond to those of an aryl nitro compound.

The symbols of the functional groups of aryl nitro compounds are given in Table 15.249. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of aryl nitro compounds are given in Tables 15.250, 15.251, and 15.252, respectively. The total energy of each aryl nitro compound given in Table 15.253 was calculated as the sum over the integer multiple of each $E_D(_{Group})$ of Table 15.252 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(_{Group})$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of aryl nitro compounds determined using Eqs. (15.79-15.108) are given in Table 15.254.

Table 15.249. The symbols of functional groups of aryl nitro compounds.

Functional Group	Group Symbol
CC (aromatic bond)	$\overset{3e}{C=C}$
CH (aromatic)	CH (i)
Aryl C-N (aniline)	$C-N$ (a)
Aryl C-N (nitro)	$C-N$ (b)
Aryl C-O	$C-O$ (a)
NO_2 group	NO_2
NH_2 group	NH_2
OH group	OH

Table 15.250. The geometrical bond parameters of aryl nitro compounds and experimental values [1].

Parameter	$\overset{3e}{C=C}$ Group	CH (i) Group	$C-N$ (a) Group	$C-N$ (b) Group	$C-O$ (a) Group	NO_2 Group	NH_2 Group	OH Group
a (a_0)	1.47348	1.60061	1.81158	1.97794	1.68220	1.33221	1.24428	1.26430
c' (a_0)	1.31468	1.03299	1.34595	1.40639	1.29700	1.15421	0.94134	0.91808
Bond Length $2c'$ $(Å)$	1.39140	1.09327	1.42449	1.48846	1.37268	1.22157	0.99627	0.971651
Exp. Bond Length $(Å)$	1.397 avg. (phenol)	1.084 (phenol)	1.431 (aniline)		1.364 (phenol)	1.224 (nitromethane)	0.998 (aniline)	0.956 (phenol)
b,c (a_0)	0.66540	1.22265	1.21254	1.39079	1.07126	0.66526	0.81370	0.86925
e	0.89223	0.64537	0.74297	0.71104	0.77101	0.86639	0.75653	0.72615

Table 15.251. The MO to HO intercept geometrical bond parameters of aryl nitro compounds. E_T is $E_T(atom-atom, msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C-H\ (C_bH)$	C_b	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$\left(C_b\overset{3e}{=}\right)_2 C_aO-H$	O	-0.74804	0	0	0		1.00000	0.87363	-15.57379		115.79	64.21	64.82	0.53799	0.38009
$\left(C_b\overset{3e}{=}\right)_2 C_a-OH$	C_a	-0.74804	-0.85035	-0.85035	0	-154.06442	0.91771	0.78762	-17.27448	-17.08362	100.00	80.00	46.39	1.16026	0.13674
$\left(C_b\overset{3e}{=}\right)_2 C_a-OH$	O	-0.74804	0	0	0		1.00000	0.87363	15.57379		106.51	73.49	51.43	1.04871	0.24829
$\left(C_b\overset{3e}{=}\right)_2 C_aOH$	C_a	-0.74804	-0.85035	-0.85035	0	-154.06442	0.91771	0.78762	-17.27448	-17.08362	133.88	46.12	58.55	0.76870	0.54598
$C\overset{3e}{=}HC_c\overset{3e}{=}C$ $C\overset{3e}{=}(H_2N)C_a\overset{3e}{=}C$ $\left(\overset{3e}{=}(H)C_b\right)_2 C_aOH$ $C\overset{3e}{=}(H_3C_a)C_b\overset{3e}{=}C$	C_c C_a C_b C_b	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533
$\left(C_b\overset{3e}{=}\right)_2 C_aNH-H$	N	-0.56690	0	0	0		0.93084	0.88392	-15.39265		121.74	58.26	67.49	0.47634	0.46500
$\left(C_b\overset{3e}{=}\right)_2 C_a-NH_2$	C_a	-0.56690	-0.85035	-0.85035	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	88.49	91.51	41.01	1.36696	0.02101
$\left(C_b\overset{3e}{=}\right)_2 C_a-NH_2$	N	-0.56690	0	0	0		0.93084	0.88392	-15.39265		96.32	83.68	46.43	1.24859	0.09736
$\left(C\overset{3e}{=}\right)_2 C_b-C_aH_3$	C_a	-0.56690	0	0	0	-152.18259	0.91771	0.88392	-15.39265	-15.20178	73.38	106.62	34.97	1.68807	0.25279
$\left(C\overset{3e}{=}\right)_2 C_b-C_aH_3$	C_b	-0.56690	-0.85035	-0.85035	0	-153.88328	0.91771	0.79597	-17.09334	-16.90247	61.56	118.44	28.27	1.81430	0.37901
$RN(O)=O$	O	-0.92918	0	0	0		1.00000	0.86359	-15.75493		135.25	44.75	66.05	0.54089	0.61333
$RN(O)=O$	N	-0.92918	-0.92918	-0.36229	0		0.93084	0.79816	-17.04640		132.36	47.64	62.44	0.61640	0.53781
$\left(C\overset{3e}{=}\right)_2 C_a-NO_2$	C_a	-0.36229	-0.85035	-0.85035	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	72.49	107.51	33.53	1.64875	0.24236
$\left(C\overset{3e}{=}\right)_2 C_a-NO_2$	N	-0.92918	-0.92918	-0.36229	0		0.93084	0.79816	-17.04640		71.53	108.47	32.98	1.65923	0.25284
$C\overset{3e}{=}(O_2N)C_a\overset{3e}{=}C$	C_a	-0.36229	-0.85035	-0.85035	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	134.65	45.35	59.47	0.74854	0.56614

Table 15.252. The energy parameters (eV) of functional groups of aryl nitro compounds.

Parameters	$\overset{3e}{C=C}$ Group	CH (i) Group	$C-N$ (a) Group	$C-N$ (b) Group	$C-O$ (a) Group	NO_2 Group	NH_2 Group	OH Group
f_1	0.75	1						
n_1	2	1	1	1	1	2	2	1
n_2	0	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	1	0
C_1	0.5	0.75	0.5	0.5	0.5	0.5	0.75	0.75
C_2	0.85252	1	1	1	1	1	0.93613	1
c_1	1	1	1	1	1	1	0.75	0.75
c_2	0.85252	0.91771	0.84665	0.91140	0.79329	0.85987	0.92171	1
c_3	0	1	0	0	0	0	0	1
c_4	3	1	2	2	2	4	1	1
c_5	0	1	0	0	0	0	2	1
C_{1o}	0.5	0.75	0.5	0.5	0.5	0.5	1.5	0.75
C_{2o}	0.85252	1	1	1	1	1	1	1
$V_e\ (eV)$	-101.12679	-37.10024	-32.76465	-31.36351	-34.04658	-106.90919	-78.97795	-40.92709
$V_p\ (eV)$	20.69825	13.17125	10.10870	9.67426	10.49024	23.57588	28.90735	14.81988
$T\ (eV)$	34.31559	11.58941	9.04312	7.92833	10.11966	40.12475	31.73641	16.18567
$V_m\ (eV)$	-17.15779	-5.79470	-4.52156	-3.96416	-5.05983	-20.06238	-15.86820	-8.09284
$E(_{AO/HO})\ (eV)$	0	-14.63489	-14.63489	-14.63489	-14.63489	0	-14.53414	-13.6181
$\Delta E_{H_2MO}(_{AO/HO})\ (eV)$	0	-1.13379	-1.13379	-0.72457	-1.49608	0	0	0
$E_T(_{AO/HO})\ (eV)$	0	-13.50110	-13.50110	-13.91032	-13.13881	0	-14.53414	-13.6181
$E(_{n_3\ AO/HO})\ (eV)$	0	0	0	0	0	0	-14.53414	0
$E_T(_{H_2MO})\ (eV)$	-63.27075	-31.63539	-31.63549	-31.63540	-31.63532	-63.27093	-48.73654	-31.63247
$E_T\left(atom-atom,msp^3.AO\right)\ (eV)$	-2.26759	-0.56690	-1.13379	-0.72457	-1.49608	-3.71673	0	0
$E_T(_{MO})\ (eV)$	-65.53833	-32.20226	-32.76916	-32.35994	-33.13145	-66.98746	-48.73660	-31.63537
$\omega\ \left(10^{15}\ rad/s\right)$	49.7272	26.4826	11.9890	17.8228	13.3984	19.0113	68.9812	44.1776
$E_K\ (eV)$	32.73133	17.43132	7.89138	11.73128	8.81907	12.51354	45.40465	29.07844
$\bar{E}_D\ (eV)$	-0.35806	-0.26130	-0.18211	-0.21927	-0.19465	-0.23440	-0.42172	-0.33749
$\bar{E}_{Kvib}\ (eV)$	0.19649 [49]	0.35532 Eq. (13.458)	0.15498 [54]	0.10539 [45]	0.12808 [19]	0.19342 [45]	0.40929 [22]	0.46311 [17-18]
$\bar{E}_{osc}\ (eV)$	-0.25982	-0.08364	-0.10462	-0.16658	-0.13061	-0.13769	-0.21708	-0.10594
$E_{mag}\ (eV)$	0.14803	0.14803	0.14803	0.14803	0.14803	0.11441	0.14803	0.11441
$E_T(_{Group})\ (eV)$	-49.54347	-32.28590	-32.87379	-32.52652	-33.26206	-67.26284	-49.17075	-31.74130
$E_{initial}(_{c_4\ AO/HO})\ (eV)$	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.53414	-13.6181
$E_{initial}(_{c_5\ AO/HO})\ (eV)$	0	-13.59844	0	0	0	0	-13.59844	-13.59844
$E_D(_{Group})\ (eV)$	5.63881	3.90454	3.60401	3.25674	3.99228	8.72329	7.43973	4.41035

Table 15.253. The total bond energies of aryl nitro compounds calculated using the functional group composition and the energies of Table 15.252 compared to the experimental values [2]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by (15.58).

Formula	Name	$\overset{3e}{C=C}$	CH (i)	$C-N$ (a) Group	$C-N$ (b) Group	$C-O$ (a) Group	NO_2 Group	NH_2 Group	OH Group	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_6H_5NO_2$	Nitrobenzene	6	5	0	1	0	1	0	0	1	65.18754	65.217	0.00046
$C_6H_4N_2O_5$	2,4-dinitrophenol	6	4	0	2	1	2	0	1	2	77.61308	77.642	0.00037
$C_6H_6N_2O_2$	2-nitroaniline	6	4	1	1	0	1	1	0	0	72.47476	72.424	-0.00070
$C_6H_6N_2O_2$	3-nitroaniline	6	4	1	1	0	1	1	0	0	72.47476	72.481	-0.00009
$C_6H_6N_2O_2$	4-nitroaniline	6	4	1	1	0	1	1	0	0	72.47476	72.476	-0.00002

Table 15.254. The bond angle parameters of aryl nitro compounds and experimental values [1]. E_T is $E_T(atom-atom, msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CCC$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	0.79232	-1.85836				120.19	120 [50-52] (benzene)
$\angle CCH$ (aromatic)																120.19		119.91	120 [50-52] (benzene)
$\angle O_aNO_b$	2.30843	2.30843	4.1231	-16.68411 O_a	24	-16.68411 O_b	24	0.81549	0.81549	1	1	1	0.81549	-1.44915				126.52	123.2 [54] (nitrobenzene) 125.3 (nitromethane)
$\angle CNO$	2.81279	2.30843	4.4159	-17.45562	40	-13.61806	O	0.77945	0.85395 (Eq. (15.114))	1	1	1	0.81670	-1.65376				118.82	118.5 [54] (nitrobenzene)
$\angle C_aOH$	2.59399	1.83616	3.6515	-14.82575	1	-14.82575	1	1	0.91771	0.75	1	0.75	0.91771	0				109.84	109.0 (phenol)
$\angle HNH$	1.88268	1.88268	3.1559	-14.53414	N	H	H	0.93613 Eq. (13.248))	1	1	1	0.75	1.06823	0				113.89	113.9 (aniline)
$\angle C_aNH$	2.69190	1.88268	3.9833	-15.95955	9	-14.53414	N	0.84665 (Eq. (15.152))	0.84665 (Eq. (15.152))	0.75	1	0.75	1.00000	0				120.05	

BENZOIC ACID COMPOUNDS

Benzoic acid compounds have a hydrogen of an aryl group replaced by a carboxylic acid group corresponding to an $C-C(O)-OH$ moiety that comprises $C=O$ and OH functional groups that are the same as those of carboxylic acids given in the corresponding section. The single bond of aryl carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. This group is also equivalent to the same group of carboxylic acids except that $\Delta E_{H_2MO}(AO/HO)$ in Eq. (15.42) and $E_T(atom-atom,msp^3.AO)$ in Eq. (15.52) are both $-1.29147\ eV$ which is a linear combination of $\frac{-1.13379\ eV}{2}$, $E_T(atom-atom,msp^3.AO)$ of the $C-H$ group that the $C-C(O)$ group replaces, and that of an independent $C2sp^3$ HO, $-0.72457\ eV$ (Eq. (14.151)).

Examples include benzoic acid, chlorobenzoic acid, and aniline carboxylic acid with formulas $C_7H_6O_2$, $C_7H_5O_2Cl$, and $C_7H_7NO_2$, respectively. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The NH_2 and $C-N$ functional groups of aniline carboxylic acids are the same as those of aniline given in the corresponding section. The $C-Cl$ functional group of 2-chlorobenzoic acids corresponding to meta substitution is equivalent to that of chlorobenzene given in the corresponding section. The $C-Cl$ functional group of 3 or 4-chlorobenzoic acids corresponding to ortho and para substitution is also equivalent to that of chlorobenzene, except that $\Delta E_{H_2MO}(AO/HO)$ in Eq. (15.42) and $E_T(atom-atom,msp^3.AO)$ in Eq. (15.52) are both $-0.92918\ eV$ (Eq. (14.513)) since each of these positions can form a resonance structure with the carboxylic acid group which is permissive of greater charge donation from the $C2sp^3$ HO.

The symbols of the functional groups of benzoic acid compounds are given in Table 15.255. The corresponding designations of benzoic acid is shown in Figure 64. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of benzoic acid compounds are given in Tables 15.256, 15.257, and 15.258, respectively. The total energy of each benzoic acid compound given in Table 15.259 was calculated as the sum over the integer multiple of

each $E_D(Group)$ of Table 15.258 corresponding to functional-group composition of the molecule. The bond angle parameters of benzoic acid compounds determined using Eqs. (15.79-15.108) are given in Table 15.260.

Table 15.255. The symbols of functional groups of benzoic acid compounds.

Functional Group	Group Symbol
CC (aromatic bond)	$C\overset{3e}{=}C$
CH (aromatic)	CH (i)
C-C(O)	$C-C(O)$
C=O (aryl carboxylic acid)	$C=O$
(O)C-O	$C-O$
OH group	OH
$Cl-C$ (Cl to aromatic bond of 2-chlorobenzoic acid)	$C-Cl$ (i)
$Cl-C$ (Cl to aromatic bond of 3 or 4-chlorobenzoic acid)	$C-Cl$ (ii)
Aryl C-N (aniline)	$C-N$
NH_2 group	NH_2

Table 15.256. The geometrical bond parameters of benzoic acid compounds and experimental values [1].

Parameter	$\overset{3e}{C=C}$ Group	CH (i) Group	$C-C(O)$ Group	$C=O$ Group	$C-O$ Group	OH Group	$C-Cl$ (i) Group	$C-Cl$ (ii) Group	$C-N$ Group	NH_2 Group
$a\ (a_0)$	1.47348	1.60061	1.95111	1.29907	1.73490	1.26430	2.20799	2.19358	1.81158	1.24428
$c'\ (a_0)$	1.31468	1.03299	1.39682	1.13977	1.31716	0.91808	1.64782	1.64243	1.34595	0.94134
Bond Length $2c'\ (Å)$	1.39140	1.09327	1.47833	1.20628	1.39402	0.971651	1.74397	1.73827	1.42449	0.99627
Exp. Bond Length $(Å)$	1.399 (benzene)	1.101 (benzene)	1.48 [55] (benzoic acid)	1.214 (acetic acid)	1.393 (methyl formate)	0.972 (formic acid)	1.737 (chlorobenzene)	1.737 (chlorobenzene)	1.431 (aniline)	0.998 (aniline)
$b,c\ (a_0)$	0.66540	1.22265	1.36225	0.62331	1.12915	0.86925	1.46967	1.45403	1.21254	0.81370
e	0.89223	0.64537	0.71591	0.87737	0.75921	0.72615	0.74630	0.74874	0.74297	0.75653

Table 15.257. The MO to HO intercept geometrical bond parameters of benzoic acid compounds. E_T is $E_T(atom-atom, msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$\overset{3e}{C}-H\ (C_bH)$	C_b	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$\overset{3e}{C}=HC_b\overset{3e}{=}C$ $\overset{3e}{C}=(HOOC_a)C_b\overset{3e}{=}C(H)_c$ $\overset{3e}{C}=(Cl)C_a\overset{3e}{=}C_b(H)$ $\overset{3e}{C}=(H_2N)C_a\overset{3e}{=}C_b(H)$	C_b C_c C_b C_b	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533
$\left(C_b\overset{3e}{=}\right)_2 C_a(O)O-H$	O	-0.92918	0	0	0		1.00000	0.86359	-15.75493		115.09	64.91	64.12	0.55182	0.36625
$\left(C_b\overset{3e}{=}\right)_2 C_a(O)-OH$	O	-0.92918	0	0	0		1.00000	0.86359	-15.75493		101.32	78.68	48.58	1.14765	0.16950
$\left(C_b\overset{3e}{=}\right)_2 C_a(O)-OH$	C_a	-0.92918	-1.34946	-0.64574	0	-154.54007	0.91771	0.76652	-17.75013	-17.55927	93.11	86.89	42.68	1.27551	0.04165
$\left(C_b\overset{3e}{=}\right)_2 C_a(OH)=O$	O	-1.34946	0	0	0		1.00000	0.84115	-16.17521		137.27	42.73	66.31	0.52193	0.61784
$\left(C_b\overset{3e}{=}\right)_2 C_a(OH)=O$	C_a	-1.34946	-0.64574	-0.92918	0	-154.54007	0.91771	0.76652	-17.75013	-17.55927	134.03	45.97	62.14	0.60699	0.53278
$C_c\overset{3e}{=}(HOOC_a)C_b\overset{3e}{=}C_c$ (C_b bound to H, Cl, or NH_2)	C_b	-0.64574	-0.85035	-0.85035	0	-153.96212	0.91771	0.79232	-17.17218	-16.98132	134.09	45.91	58.79	0.76344	0.55124
$\left(\overset{3e}{C=}\right)_2 C_a-Cl$	Cl	-0.36229	0	0	0		1.05158	0.89582	15.18804		82.92	97.08	37.22	1.75824	0.11042
$\left(\overset{3e}{C=}\right)_2 C_a-Cl$	C_a	-0.36229	-0.85035	-0.85035	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	73.32	106.68	31.67	1.87911	0.23129
$C_b\overset{3e}{=}(Cl)C_a\overset{3e}{=}C_b$ (C_b bound to H or Cl)	C_a	-0.36229	-0.85035	-0.85035	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	134.65	45.35	59.47	0.74854	0.56614
$\left(C_b\overset{3e}{=}\right)_2 C_aNH-H$	N	-0.56690	0	0	0		0.93084	0.88392	-15.39265		121.74	58.26	67.49	0.47634	0.46500
$\left(C_b\overset{3e}{=}\right)_2 C_a-NH_2$	C_a	-0.56690	-0.85035	-0.85035	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	88.49	91.51	41.01	1.36696	0.02101
$\left(C_b\overset{3e}{=}\right)_2 C_a-NH_2$	N	-0.56690	0	0	0		0.93084	0.88392	-15.39265		96.32	83.68	46.43	1.24859	0.09736
$\overset{3e}{C}=(H_2N)C_a\overset{3e}{=}C$	C_a	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533

Table 15.258. The energy parameters (eV) of functional groups of benzoic acid compounds.

Parameters	$C\overset{3e}{=}C$ Group	CH (i) Group	$C-C(O)$ Group	$C=O$ Group	$C-O$ Group	OH Group	$C-Cl$ (i) Group	$C-Cl$ (ii) Group	$C-N$ Group	NH_2 Group
f_1	0.75	1								
n_1	2	1	1	2	1	1	1	1	1	2
n_2	0	0	0	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	1
C_1	0.5	0.75	0.5	0.5	0.5	0.75	0.5	0.5	0.5	0.75
C_2	0.85252	1	1	1	1	1	0.81317	0.81317	1	0.93613
c_1	1	1	1	1	1	0.75	1	1	1	0.75
c_2	0.85252	0.91771	0.91771	0.85395	0.85395	1	1	1	0.84665	0.92171
c_3	0	1	0	2	0	1	0	0	0	0
c_4	3	1	2	4	2	1	2	2	2	1
c_5	0	1	0	0	0	1	0	0	0	2
C_{1o}	0.5	0.75	0.5	0.5	0.5	0.75	0.5	0.5	0.5	1.5
C_{2o}	0.85252	1	1	1	1	1	0.81317	0.81317	1	1
$V_e\ (eV)$	-101.12679	-37.10024	-32.15216	-111.25473	-35.08488	-40.92709	-31.85648	-32.14474	-32.76465	-78.97795
$V_p\ (eV)$	20.69825	13.17125	9.74055	23.87467	10.32968	14.81988	8.25686	8.28394	10.10870	28.90735
$T\ (eV)$	34.31559	11.58941	8.23945	42.82081	10.11150	16.18567	7.21391	7.32700	9.04312	31.73641
$V_m\ (eV)$	-17.15779	-5.79470	-4.11973	-21.41040	-5.05575	-8.09284	-3.60695	-3.66350	-4.52156	-15.86820
$E(AO/HO)\ (eV)$	0	-14.63489	-14.63489	0	-14.63489	-13.6181	-14.63489	-14.63489	-14.63489	-14.53414
$\Delta E_{H_2MO}(AO/HO)\ (eV)$	0	-1.13379	-1.29147	-2.69893	-2.69893	0	-2.99216	-2.99216	-1.13379	0
$E_T(AO/HO)\ (eV)$	0	-13.50110	-13.34342	2.69893	-11.93596	-13.6181	-11.64273	-11.64273	-13.50110	-14.53414
$E(n,AO/HO)\ (eV)$	0	0	0	0	0	0	0	0	0	-14.53414
$E_T(H_2MO)\ (eV)$	-63.27075	-31.63539	-31.63530	-63.27074	-31.63541	-31.63247	-31.63539	-31.63542	-31.63549	-48.73654
$E_T(atom-atom,msp^3.AO)\ (eV)$	-2.26759	-0.56690	-1.29147	-2.69893	-1.85836	0	-0.72457	-0.92918	-1.13379	0
$E_T(MO)\ (eV)$	-65.53833	-32.20226	-32.92684	-65.96966	-33.49373	-31.63537	-32.35994	-32.56455	-32.76916	-48.73660
$\omega\ (10^{15}\ rad/s)$	49.7272	26.4826	10.7262	59.4034	24.3637	44.1776	8.03459	8.11389	11.9890	68.9812
$E_K\ (eV)$	32.73133	17.43132	7.06019	39.10034	16.03660	29.07844	5.28851	5.34070	7.89138	45.40465
$\bar{E}_D\ (eV)$	-0.35806	-0.26130	-0.17309	-0.40804	-0.26535	-0.33749	-0.14722	-0.14888	-0.18211	-0.42172
$\bar{E}_{Kvib}\ (eV)$	0.19649 [49]	0.35532 Eq. (13.458)	0.10502 [29]	0.21077 [12]	0.14010 [31]	0.46311 [17-18]	0.08059 [12]	0.08059 [12]	0.15498 [54]	0.40929 [22]
$\bar{E}_{osc}\ (eV)$	-0.25982	-0.08364	-0.12058	-0.30266	-0.19530	-0.10594	-0.10693	-0.10859	-0.10462	-0.21708
$E_{mag}\ (eV)$	0.14803	0.14803	0.14803	0.11441	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803
$E_T(Group)\ (eV)$	-49.54347	-32.28590	-33.04742	-66.57498	-33.68903	-31.74130	-32.46687	-32.67314	-32.87379	-49.17075
$E_{initial}(c_4\ AO/HO)\ (eV)$	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-13.6181	-14.63489	-14.63489	-14.63489	-14.53414
$E_{initial}(c_5\ AO/HO)\ (eV)$	0	-13.59844	0	0	0	-13.59844	0	0	0	-13.59844
$E_D(Group)\ (eV)$	5.63881	3.90454	3.77764	7.80660	4.41925	4.41035	3.19709	3.40336	3.60401	7.43973

Table 15.259. The total bond energies of benzoic acid compounds calculated using the functional group composition and the energies of Table 15.258 compared to the experimental values [2].

Formula	Name	$\overset{3e}{C=C}$ Group	CH (i) Group	$C-C(O)$ Group	$C=O$ Group	$C-O$ Group	OH Group	$C-Cl$ (i) Group	$C-Cl$ (ii) Group	$C-N$ Group	NH_2 Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_7H_6O_2$	Benzoic acid	6	5	1	1	1	1	0	0	0	0	73.76938	73.762	-0.00009
$C_7H_5ClO_2$	2-chlorobenzoic acid	6	4	1	1	1	1	1	0	0	0	73.06193	73.082	0.00027
$C_7H_5ClO_2$	3-chlorobenzoic acid	6	4	1	1	1	1	0	1	0	0	73.26820	73.261	-0.00010
$C_7H_5ClO_2$	4-chlorobenzoic acid	6	4	1	1	1	1	0	1	0	0	73.26820	73.247	-0.00028
$C_7H_7NO_2$	Aniline-2-carboxylic acid	6	4	1	1	1	1	0	0	1	1	80.90857	80.941	0.00041
$C_7H_7NO_2$	Aniline-3-carboxylic acid	6	4	1	1	1	1	0	0	1	1	80.90857	80.813	-0.00118
$C_7H_7NO_2$	Aniline-4-carboxylic acid	6	4	1	1	1	1	0	0	1	1	80.90857	80.949	0.00050

Table 15.260. The bond angle parameters of benzoic acid compounds and experimental values [1]. E_T is $E_T(atom-atom, msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CCC$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	0.79232	-1.85836				120.19	120 [50-52] (benzene)
$\angle CCH$ (aromatic)																120.19		119.91	120 [50-52] (benzene)
$\angle C_aO_bH$	2.63431	1.83616	3.6405	-14.82575	1	-14.82575	1	1	0.91771	0.75	1	0.75	0.91771	0				107.71	
$\angle C_bC_aO_a$	2.82796	2.27954	4.4721	-17.17218	34	-13.61806	O	0.79232	0.85395 (Eq. (15.114))	1	1	1	0.82313	-1.65376				121.86	122 [55] (benzoic acid)
$\angle C_bC_aO_b$	2.82796	2.63431	4.6690	-16.40067	19	-13.61806	O	0.82959	0.85395 (Eq. (15.114))	1	1	1	0.84177	-1.65376				117.43	118 [55] (benzoic acid)
$\angle O_aC_aO_b$	2.27954	2.63431	4.3818	-16.17521 O_a	12	-15.75493 O_b	7	0.84115	0.86359	1	1	1	0.85237	-1.44915				126.03	122 [55] (benzoic acid)
$\angle CCC$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	0.79232	-1.85836				120.19	120 $(\angle CC(H)C$ chlorobenzene) 121.7 $(\angle CC(Cl)C$ chlorobenzene) 120 [50-52] (benzene)
$\angle CCH$ $\angle CCCl$ (aromatic)																120.19		119.91	120 [50-52] (benzene)
$\angle HNH$	1.88268	1.88268	3.1559	-14.53414	N	H	H	0.93613 Eq. (13.248))	1	1	1	0.75	1.06823	0				113.89	113.9 (aniline)
$\angle C_aNH$	2.69190	1.88268	3.9833	-15.95955	9	-14.53414	N	0.84665 (Eq. (15.152))	0.84665 (Eq. (15.152))	0.75	1	0.75	1.00000	0				120.05	

ANISOLE

Anisole has the formula C_7H_8O and comprises the phenol molecule with the hydroxyl hydrogen atom replaced by the moiety $-O-CH_3$ to form an ether comprising aromatic and methyl functional groups as well as two types of $C-O$ functional groups, one for aryl carbon to oxygen and one for methyl carbon to oxygen. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The CH_3 and methyl $C-O$ functional groups are the same as those of the corresponding ether groups given in the corresponding section.

The $C-O$ functional group comprising the bond between the ether oxygen and aromatic ring is equivalent to that of the methyl ether $C-O$ functional group except that $\Delta E_{H_2MO}(AO/HO)$ in Eq. (15.42) and $E_T(atom-atom,msp^3.AO)$ in Eq. (15.52) are both $-1.13379\ eV$ (Eq. (14.247)). $E_T(atom-atom,msp^3.AO)$ is based on the energy match between the OCH_3 group and the $C2sp^3$ HO of the aryl group and is twice that of the aryl $C-H$ group that it replaces.

The symbols of the functional groups of anisole are given in Table 15.261. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of anisole are given in Tables 15.262, 15.263, and 15.264, respectively. The total energy of anisole given in Table 15.265 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.264 corresponding to functional-group composition of the molecule. The bond angle parameters of anisole determined using Eqs. (15.79-15.108) are given in Table 15.266.

Table 15.261. The symbols of functional groups of anisole.

Functional Group	Group Symbol
CC (aromatic bond)	$C\overset{3e}{=}C$
CH (aromatic)	CH (i)
Aryl C-O	$C-O$ (a)
Methyl C-O	$C-O$ (b)
CH_3 group	$C-H\ (CH_3)$

Table 15.262. The geometrical bond parameters of anisole and experimental values [1].

Parameter	$C\overset{3e}{=}C$ Group	$C'H$ (i) Group	$C'-O$ (a) Group	$C-O$ (b) Group	$C-H\ (CH_3)$ Group
$a\ (a_0)$	1.47348	1.60061	1.82682	1.80717	1.64920
$c'\ (a_0)$	1.31468	1.03299	1.35160	1.34431	1.04856
Bond Length $2c'$ (Å)	1.39140	1.09327	1.43047	1.42276	1.10974
Exp. Bond Length (Å)	1.397 avg. (phenol)	1.084 (phenol)			1.11 (avg.) (toluene)
$b,c\ (a_0)$	0.66540	1.22265	1.22900	1.20776	1.27295
e	0.89223	0.64537	0.73986	0.74388	0.63580

Table 15.263. The MO to HO intercept geometrical bond parameters of anisole. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C'-H\ (C_bH)$	C'_b	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$C'-H\ (OC'_cH_3)$	C_c	-0.72457	0	0	0	-152.34026	0.91771	0.87495	-15.55033	-15.35946	78.85	101.15	42.40	1.21777	0.16921
$\left(C_b\overset{3e}{=}\right)_2 C_aO-C_cH_3$	C_c	-0.72457	0	0	0	-152.34026	0.91771	0.87495	-15.55033	-15.35946	95.98	84.02	46.10	1.25319	0.09112
$\left(C_b\overset{3e}{=}\right)_2 C_aO-C_cH_3$	O	-0.72457	-0.56690	0	0		1.00000	0.84418	-16.11722		93.38	86.62	44.25	1.29456	0.04975
$\left(C_b\overset{3e}{=}\right)_2 C_a-OC_cH_3$	C_a	-0.56690	-0.85035	-0.85035	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	87.00	93.00	40.30	1.39329	0.04170
$\left(C_b\overset{3e}{=}\right)_2 C_a-OC_cH_3$	O	-0.56690	-0.72457	0	0		1.00000	0.84418	-16.11722		91.59	88.41	43.36	1.32814	0.02346
$\left(C_b\overset{3e}{=}\right)_2 C'_aOC'_cH_3$	C'_a	-0.56690	-0.85035	-0.85035	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533
$\left(\overset{3e}{=}(H)C'_b\right)_2 C_aOC'_cH_3$	C'_b	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533

Table 15.264. The energy parameters (eV) of functional groups of anisole.

Parameters	$\overset{3e}{C=C}$ Group	CH (i) Group	$C-O$ (a) Group	$C-O$ (b) Group	CH_3 Group
f_1	0.75	1			
n_1	2	1	1	1	3
n_2	0	0	0	0	2
n_3	0	0	0	0	0
C_1	0.5	0.75	0.5	0.5	0.75
C_2	0.85252	1	1	1	1
c_1	1	1	1	1	1
c_2	0.85252	0.91771	0.85395	0.85395	0.91771
c_3	0	1	0	0	0
c_4	3	1	2	2	1
c_5	0	1	0	0	3
C_{1o}	0.5	0.75	0.5	0.5	0.75
C_{2o}	0.85252	1	1	1	1
$V_e\ (eV)$	-101.12679	-37.10024	-32.67197	-33.15757	-107.32728
$V_p\ (eV)$	20.69825	13.17125	10.06645	10.12103	38.92728
$T\ (eV)$	34.31559	11.58941	8.94231	9.17389	32.53914
$V_m\ (eV)$	-17.15779	-5.79470	-4.47115	-4.58695	-16.26957
$E(AO/HO)\ (eV)$	0	-14.63489	-14.63489	-14.63489	-15.56407
$\Delta E_{H_2MO}(AO/HO)\ (eV)$	0	-1.13379	-1.13379	-1.44915	0
$E_T(AO/HO)\ (eV)$	0	-13.50110	-13.50110	-13.18574	-15.56407
$E_T(H_2MO)\ (eV)$	-63.27075	-31.63539	-31.63547	-31.63533	-67.69451
$E_T\left(atom-atom, msp^3.AO\right)\ (eV)$	-2.26759	-0.56690	-1.13379	-1.44915	0
$E_T(MO)\ (eV)$	-65.53833	-32.20226	-32.76916	-33.08452	-67.69450
$\omega\ \left(10^{15}\ rad/s\right)$	49.7272	26.4826	11.8393	12.0329	24.9286
$E_K\ (eV)$	32.73133	17.43132	7.79284	7.92028	16.40846
$\bar{E}_D\ (eV)$	-0.35806	-0.26130	-0.18097	-0.18420	-0.25352
$\bar{E}_{Kvib}\ (eV)$	0.19649 [49]	0.35532 Eq. (13.458)	0.13663 [21]	0.13663 [21]	0.35532 (Eq. (13.458))
$\bar{E}_{osc}\ (eV)$	-0.25982	-0.08364	-0.11266	-0.11589	-0.22757
$E_{mag}\ (eV)$	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(Group)\ (eV)$	-49.54347	-32.28590	-32.88182	-33.20040	-67.92207
$E_{initial}(c_4\ AO/HO)\ (eV)$	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(c_5\ AO/HO)\ (eV)$	0	-13.59844	0	0	-13.59844
$E_D(Group)\ (eV)$	5.63881	3.90454	3.61204	3.93062	12.49186

Table 15.265. The total bond energies of anisole calculated using the functional group composition and the energies of Table 15.264 compared to the experimental values [2].

Formula	Name	$\overset{3e}{C=C}$	CH (i)	$C-O$ (a) Group	$C-O$ (b) Group	CH_3 Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_7H_8O	Anisole	6	5	1	1	1	73.39006	73.355	-0.00047

Table 15.266. The bond angle parameters of anisole and experimental values [1]. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CCC$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	0.79232	-1.85836				120.19	120 [50-52] (benzene)
$\angle CCH$ (aromatic)																120.19		119.91	120 [50-52] (benzene)

PYRROLE

Pyrrole having the formula C_4H_5N comprises the conjugated alkene 1,3-butdiene that forms a cyclic structure by terminal-atom bonding to a NH functional group. The two symmetrical carbon-to-nitrogen bonds comprise the $C-N-C$ functional group. The 1,3-butdiene moiety comprises $C-C$, $C=C$, and CH functional groups. The $C-C$ and $C=C$ groups are equivalent to the corresponding groups of 1,3-butdiene given in the Cyclic and Conjugated Alkenes section except that the energies terms of the corresponding to oscillation in the transition state match pyrrole. Furthermore, the conjugated double bonds have the same bonding as in 1,3-butdiene except that the hybridization terms c_2 of the $C-C$ and $C=C$ groups and C_2 and C_{2o} of the $C=C$ group in Eqs. (15.42) and (15.52) become that of benzene given by Eq. (15.143), ($C_2\left(benzeneC2sp^3HO\right)=c_2\left(benzeneC2sp^3HO\right)=0.85252$), in the cyclic pyrrole MO which has aromatic character. The bonding in pyrrole, furan, and thiophene are the same except for the energy match to the corresponding heteroatoms. The hybridization permits double-bond character in the carbon-heteroatom bonding.

The NH group is solved equivalently to that of a secondary amine as given in the corresponding section except that the hybridization term c_2 is that of the amino group of aniline in order provide double-bond character to match the group to the other orbitals of the molecule. Similarly, the CH functional group is equivalent to that of 1,3-butdiene, except that $\Delta E_{H_2MO}\left(AO/HO\right)=-2.26758\ eV$ (Eq. (14.247)) in Eq. (15.42) in order to provide matching double-bond character.

The solution of the $C-N-C$ functional group comprises the hybridization of the $2s$ and $2p$ AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs and the nitrogen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. Thus, the $C-N-C$-bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with $n_1=2$ in Eqs. (15.42) and (15.52). The hybridization factor $c_2\left(arylC2sp^3HO\ to\ N\right)=0.84665$ (Eq. (15.152)) matches the double-bond character of the $C2sp^3$ HOs to the N atom of the NH group, and C_2 and C_{2o} in Eqs. (15.42) and (15.52)

become that of benzene given by Eq. (15.143), $C_2(benzeneC2sp^3HO) = 0.85252$. Furthermore, $\Delta E_{H_2MO}(AO/HO)$ in Eq. (15.42) and $E_T(atom-atom,msp^3.AO)$ in Eq. (15.52) are both $-0.92918\ eV$ (Eq. (14.513)) per atom corresponding to $-3.71673\ eV$ in total. This is the maximum energy for a single bond and corresponds to methylene character as given in the Continuous-Chain Alkanes section.

The symbols of the functional groups of pyrrole are given in Table 15.267. The structure of pyrrole is shown in Figure 65. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of pyrrole are given in Tables 15.268, 15.269, and 15.270, respectively. The total energy of pyrrole given in Table 15.271 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.270 corresponding to functional-group composition of the molecule. The bond angle parameters of pyrrole determined using Eqs. (15.79-15.108) are given in Table 15.272.

Table 15.267. The symbols of functional groups of pyrrole.

Functional Group	Group Symbol
$C_a = C_b$ double bond	$C=C$
$C_b - C_b$	$C-C$
$C_a - N - C_a$	$C-N-C$
NH group	NH
CH	CH

Table 15.268. The geometrical bond parameters of pyrrole and experimental values [1].

Parameter	$C=C$ Group	$C-C$ Group	$C-N-C$ Group	NH Group	CH Group
$a\ (a_0)$	1.45103	1.77965	1.43222	1.24428	1.53380
$c'\ (a_0)$	1.30463	1.33404	1.29614	0.94134	1.01120
Bond Length $2c'\ (Å)$	1.38076	1.41188	1.37178	0.996270	1.07021
Exp. Bond Length $(Å)$	1.382 (pyrrole)	1.417 (pyrrole)	1.370 (pyrrole)	0.996 (pyrrole)	1.076 (pyrrole)
$b,c\ (a_0)$	0.63517	1.17792	0.60931	0.81370	1.15326
e	0.89910	0.74961	0.90499	0.75653	0.65928

Table 15.269. The MO to HO intercept geometrical bond parameters of pyrrole. R_1 is an alkyl group and R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C-H\ (C_aH)$	C_a	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	83.35	96.65	43.94	1.10452	0.09331
$C-H\ (C_bH)$	C_b	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	82.21	97.79	43.14	1.11914	0.10794
$C_a=(H)C_b-C_b(H)=C_a$	C_b	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	91.57	88.43	42.49	1.31226	0.02177
$C_a=C_b(H)(H)C_b=C_a$	C_b	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	136.36	43.64	59.86	0.72857	0.57606
$HNC_a=C_b(H)$	C_a	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	136.75	43.25	60.35	0.71784	0.58678
$C_a(H)N-C_a=C_b(H)$	C_a	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	138.54	41.46	61.09	0.69238	0.60376
$C_a(H)N-C_a=C_b(H)$	N	-0.92918	-0.92918	0	0		0.93084	0.81549	-16.68411		138.92	41.08	61.59	0.68147	0.61467
$N-H\ (NH)$	N	-0.92918	-0.92918	0	0		0.93084	0.81549	-16.68411		117.34	62.66	62.90	0.56678	0.57456

Table 15.270. The energy parameters (eV) of functional groups of pyrrole.

Parameters	$C=C$ Group	$C-C$ Group	$C-N-C$ Group	NH Group	CH Group
n_1	2	1	2	1	1
n_2	0	0	0	0	0
n_3	0	0	0	0	0
C_1	0.5	0.5	0.5	0.75	0.75
C_2	0.85252	1	0.85252	0.93613	1
c_1	1	1	1	0.75	1
c_2	0.85252	0.85252	0.84665	0.92171	0.91771
c_3	0	0	0	1	1
c_4	4	2	4	1	1
c_5	0	0	0	1	1
C_{1o}	0.5	0.5	0.5	0.75	0.75
C_{2o}	0.85252	1	0.85252	1	1
$V_e\ (eV)$	-104.37986	-33.80733	-106.58684	-39.48897	-39.09538
$V_p\ (eV)$	20.85777	10.19898	20.99432	14.45367	13.45505
$T\ (eV)$	35.96751	9.49831	37.21047	15.86820	12.74462
$V_m\ (eV)$	-17.98376	-4.74915	-18.60523	-7.93410	-6.37231
$E(AO/HO)\ (eV)$	0	-14.63489	0	-14.53414	-14.63489
$\Delta E_{H_2MO}(AO/HO)\ (eV)$	-2.26759	-1.85836	-3.71673	0	-2.26758
$E_T(AO/HO)\ (eV)$	2.26759	-12.77653	3.71673	-14.53414	-12.36731
$E_T(H_2MO)\ (eV)$	-63.27075	-31.63572	-63.27056	-31.63534	-31.63533
$E_T\left(atom-atom, msp^3.AO\right)\ (eV)$	-2.26759	-2.26759	-3.71673	0	0
$E_T(MO)\ (eV)$	-65.53833	-33.90295	-66.98746	-31.63537	-31.63537
$\omega\ \left(10^{15}\ rad/s\right)$	15.4421	12.3131	15.7474	48.7771	28.9084
$E_K\ (eV)$	10.16428	8.10471	10.36521	32.10594	19.02803
$\bar{E}_D\ (eV)$	-0.20668	-0.19095	-0.21333	-0.35462	-0.27301
$\bar{E}_{Kvib}\ (eV)$	0.17897 [6]	0.14829 [48]	0.11159 [12]	0.40696 [24]	0.39427 [56]
$\bar{E}_{osc}\ (eV)$	-0.11720	-0.11680	-0.15754	-0.15115	-0.07587
$E_{mag}\ (eV)$	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(Group)\ (eV)$	-65.77272	-34.01976	-67.30254	-31.78651	-31.71124
$E_{initial}(c_4\ AO/HO)\ (eV)$	-14.63489	-14.63489	-14.63489	-14.53414	-14.63489
$E_{initial}(c_5\ AO/HO)\ (eV)$	0	0	0	-13.59844	-13.59844
$E_D(Group)\ (eV)$	7.23317	4.74998	8.76298	3.51208	3.32988

Table 15.271. The total bond energies of pyrrole calculated using the functional group composition and the energies of Table 15.270 compared to the experimental values [2].

Formula	Name	$C=C$	$C-C$	$C-N-C$	NH	CH	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_4H_5N	Pyrrole	2	1	1	1	4	44.81090	44.785	-0.00057

Table 15.272. The bond angle parameters of pyrrole and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.B)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.B)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HC'_aN$	2.02241	2.59228	4.0166	-14.82575	1	-14.53414	N	0.91771	0.92171 Eq. (15.151))	0.75	1	0.75	1.00435	0				120.51	121.5 (pyrrole)
$\angle C_bC_aH_a$																120.51	107.52	131.97	
$\angle HNC'_a$	1.88268	2.59228	3.8987	-14.53414	N	-16.49325	6	0.84665 (Eq. (15.152))	0.82493 (Eq. (15.64))	0.75	1	0.75	0.97435	0				120.37	
$\angle H_bC'_bC'_b$	2.02241	2.66807	4.2111	-16.88873 C'_b	15	-15.95954 C'_b	6	0.80561	0.85252	0.75	1	0.75	1.05822	0				127.20	127.1 (pyrrole)
$\angle H_aC_aC_b$	2.02241	2.60925	4.2111	-16.88873 C'_a	15	-15.95954 C_b	6	0.80561	0.85252	0.75	1	0.75	1.05822	0				130.36	
$\angle H_bC_bC'_a$	2.02241	2.60925	4.1312	-17.09334 C'_b	18	-16.47951 C'_a	11	0.79597	0.82562	0.75	1	0.75	1.03725	0				125.76	
$\angle C'_bC_bH_b$																125.76	107.01	127.23	127.1 (pyrrole)
$\angle NC'_aC_b$	2.59228	2.60925	4.1952	-14.53414	N	-17.09334 C'_b	18	0.84665 (Eq (15.152))	0.79597	1	1	1	0.82131	-1.44915				107.52	107.7 (pyrrole)
$\angle C'_aNC'_a$	2.59228	2.59228	4.2426	-17.81791	26	-17.81791	26	0.76360	0.76360	1	1	1	0.76360	-1.85836				109.83	109.8 (pyrrole)
$\angle C'_aC'_bC'_b$	2.60925	2.66807	4.2426	-17.81791	26	-18.02252	29	0.76360	0.75493	1	1	1	0.75927	-1.85836				107.01	107.4 (pyrrole)

FURAN

Furan having the formula C_4H_4O comprises the conjugated alkene 1,3-butdiene that forms a cyclic structure by terminal-atom bonding to an oxygen atom. The two symmetrical carbon-to-oxygen bonds comprise the $C-O-C$ functional group. The 1,3-butdiene moiety comprises $C-C$, $C=C$, and CH functional groups. The CH, $C-C$, and $C=C$ groups are equivalent to the corresponding groups of pyrrole given in the corresponding section.

The $C-O-C$ functional group of furan is solved in a similar manner as that of the $C-N-C$ group of pyrrole. The solution of the $C-O-C$ functional group comprises the hybridization of the $2s$ and $2p$ AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs and the oxygen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. Thus, the $C-O-C$-bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with $n_1 = 2$ in Eqs. (15.42) and (15.52). The hybridization factor $c_2\left(arylC2sp^3HO\ to\ O\right) = 0.79329$ (Eq. (15.150)) matches the double-bond character of the $C2sp^3$ HOs to the O atom, and C_2 and C_{2o} in Eqs. (15.42) and (15.52) become that of benzene given by Eq. (15.143), $C_2\left(benzeneC2sp^3HO\right) = 0.85252$. Furthermore, $E_T\left(atom-atom, msp^3.AO\right)$ in Eq. (15.52) is $-0.92918\ eV$ (Eq. (14.513)) per atom corresponding to $-3.71673\ eV$ in total.

The symbols of the functional groups of furan are given in Table 15.273. The structure of furan is shown in Figure 66. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of furan are given in Tables 15.274, 15.275, and 15.276, respectively. The total energy of furan given in Table 15.277 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.276 corresponding to functional-group composition of the molecule. The bond angle parameters of furan determined using Eqs. (15.79-15.108) are given in Table 15.278.

Table 15.273. The symbols of functional groups of furan.

Functional Group	Group Symbol
$C_a=C_b$ double bond	$C=C$
C_b-C_b	$C-C$
C_a-O-C_a	$C-O-C$
CH	CH

Table 15.274. The geometrical bond parameters of furan and experimental values [1].

Parameter	$C=C$ Group	$C-C$ Group	$C-O-C$ Group	CH Group
$a\ (a_0)$	1.45103	1.77965	1.41546	1.53380
$c'\ (a_0)$	1.30463	1.33404	1.28854	1.01120
Bond Length $2c'\ (Å)$	1.38076	1.41188	1.36373	1.07021
Exp. Bond Length $(Å)$	1.361 (furan)	1.431 (furan)	1.362 (furan)	1.075 (furan)
$b,c\ (a_0)$	0.63517	1.17792	0.58583	1.15326
e	0.89910	0.74961	0.91033	0.65928

Table 15.275. The MO to HO intercept geometrical bond parameters of furan. R_1 is an alkyl group and R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C-H\ (C_aH)$	C_a	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	83.35	96.65	43.94	1.10452	0.09331
$C-H\ (C_bH)$	C_b	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	82.21	97.79	43.14	1.11914	0.10794
$C_a=(H)C_b-C_b(H)=C_a$	C_b	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	91.57	88.43	42.49	1.31226	0.02177
$C_a=C_b(H)(H)C_b=C_a$	C_b	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	136.36	43.64	59.86	0.72857	0.57606
$OC_a=C_b(H)$	C_a	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	136.75	43.25	60.35	0.71784	0.58678
$C_aO-C_a=C_b(H)$	C_a	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	140.16	39.84	61.75	0.66992	0.61862
$C_aO-C_a=C_b(H)$	O	-0.92918	-0.92918	0	0		1.00000	0.81549	-16.68411		140.52	39.48	62.25	0.65906	0.62947

Table 15.276. The energy parameters (eV) of functional groups of furan.

Parameters	$C=C$ Group	$C-C$ Group	$C-O-C$ Group	CH Group
n_1	2	1	2	1
n_2	0	0	0	0
n_3	0	0	0	0
C_1	0.5	0.5	0.5	0.75
C_2	0.85252	1	0.85252	1
c_1	1	1	1	1
c_2	0.85252	0.85252	0.79329	0.91771
c_3	0	0	0	1
c_4	4	2	4	1
c_5	0	0	0	1
C_{1o}	0.5	0.5	0.5	0.75
C_{2o}	0.85252	1	0.85252	1
$V_e\ (eV)$	-104.37986	-33.80733	-102.49036	-39.09538
$V_p\ (eV)$	20.85777	10.19898	21.11822	13.45505
$T\ (eV)$	35.96751	9.49831	36.20391	12.74462
$V_m\ (eV)$	-17.98376	-4.74915	-18.10196	-6.37231
$E(_{AO/HO})\ (eV)$	0	-14.63489	0	-14.63489
$\Delta E_{H_2MO}(_{AO/HO})\ (eV)$	-2.26759	-1.85836	0	-2.26758
$E_T(_{AO/HO})\ (eV)$	2.26759	-12.77653	0	-12.36731
$E_T(_{H_2MO})\ (eV)$	-63.27075	-31.63572	-63.27019	-31.63533
$E_T(atom-atom, msp^3.AO)\ (eV)$	-2.26759	-2.26759	-3.71673	0
$E_T(_{MO})\ (eV)$	-65.53833	-33.90295	-66.98746	-31.63537
$\omega\ (10^{15}\ rad/s)$	15.4421	12.3131	58.0664	28.9084
$E_K\ (eV)$	10.16428	8.10471	38.22034	19.02803
$\bar{E}_D\ (eV)$	-0.20668	-0.19095	-0.40965	-0.27301
$\bar{E}_{Kvib}\ (eV)$	0.17897 [6]	0.14829 [48]	0.12523 [57]	0.39427 [56]
$\bar{E}_{osc}\ (eV)$	-0.11720	-0.11680	-0.34704	-0.07587
$E_{mag}\ (eV)$	0.14803	0.14803	0.14803	0.14803
$E_T(_{Group})\ (eV)$	-65.77272	-34.01976	-67.68154	-31.71124
$E_{initial}(_{c_4\ AO/HO})\ (eV)$	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(_{c_5\ AO/HO})\ (eV)$	0	0	0	-13.59844
$E_D(_{Group})\ (eV)$	7.23317	4.74998	9.14198	3.32988

Table 15.277. The total bond energies of furan calculated using the functional group composition and the energies of Table 15.276 compared to the experimental values [2].

Formula	Name	$C=C$	$C-C$	$C-O-C$	CH	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C4H4O	Furan	2	1	1	4	41.67782	41.692	0.00033

Table 15.278. The bond angle parameters of furan and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom, msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.B)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.B)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HC_aO$	2.02241	2.57707	3.9328	-16.88873	15	-13.61806	0	0.80561	0.79329 Eq. (15.150))	0.75	1	0.75	0.98470	0				117.02	115.9 (furan)
$\angle C_bC_aH_a$																117.02	110.69	132.29	
$\angle H_bC_bC_b$	2.02241	2.66807	4.2269	-16.88873 C_b	15	-15.95954 C_b	6	0.80561	0.85252	0.75	1	0.75	1.05822	0				128.09	128.0 (furan)
$\angle H_aC_aC_b$	2.02241	2.60925	4.2269	-16.88873 C_a	15	-15.95954 C_b	6	0.80561	0.85252	0.75	1	0.75	1.05822	0				131.32	
$\angle H_bC_bC_a$	2.02241	2.60925	4.1312	-17.09334 C_b	18	-16.47951 C_a	11	0.79597	0.82562	0.75	1	0.75	1.03725	0				125.76	
$\angle C_bC_bH_b$																125.76	107.01	127.23	128.0 (furan)
$\angle C_bC_aO$	2.60925	2.57707	4.2661	-17.09334 C_b	18	-13.61806	0	0.79597	0.79329 Eq. (15.150))	1	1	1	0.79463	-1.65376				110.69	110.7 (furan)
$\angle C_aOC_a$	2.57707	2.57707	4.1231	-18.22713	30	-18.22713	30	0.74646	0.74646	1	1	1	0.74646	-1.85836				106.25	106.6 (furan)
$\angle C_aC_bC_b$	2.60925	2.66807	4.2426	-17.81791	26	-18.02252	29	0.76360	0.75493	1	1	1	0.75927	-1.85836				107.01	106.1 (furan)

THIOPHENE

Thiophene having the formula C_4H_4S comprises the conjugated alkene 1,3-butdiene that forms a cyclic structure by terminal-atom bonding to an oxygen atom. The two symmetrical carbon-to-oxygen bonds comprise the $C-S-C$ functional group. The 1,3-butdiene moiety comprises $C-C$, $C=C$, and CH functional groups. The CH, $C-C$, and $C=C$ groups are equivalent to the corresponding groups of pyrrole and furan given in the corresponding sections.

The $C-S-C$ functional group of thiophene is solved in a similar manner as that of the $C-N-C$ group of pyrrole and the $C-O-C$ group of furan. The solution of the $C-S-C$ functional group comprises the hybridization of the $2s$ and $2p$ AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs and the oxygen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. Thus, the $C-S-C$-bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with $n_1 = 2$ in Eqs. (15.42) and (15.52).

In thiophene, the energy of sulfur is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_2 in Eq. (15.52) is $c_2(benzeneC2sp^3HO) = 0.85252$ to match the double-bond character of the $C2sp^3$ HOs, and the energy matching condition is further determined by the C_2 parameter. Using the energy of S, $E(S) = -10.36001\ eV$ in Eq. (15.68) and the $C2sp^3$ HO energy of $E(C,2sp^3) = -15.76868\ eV$ (Eq. (15.18) corresponding to $s=2$ in Eqs. (15.18-15.20), the hybridization factor C_2 of Eq. (15.52) for the $C-S-C$-bond MO is

$$C_2(S3p\ to\ \text{aryl-type}\ C2sp^3HO) = \frac{E(S,3p)}{E(C,2sp^3)} = \frac{-10.36001\ eV}{-15.76868\ eV} = 0.65700 \tag{15.153}$$

C_{1o} is also given by Eq. (15.153). Furthermore, $\Delta E_{H_2MO}(AO/HO)$ of the $C-S-C$-bond MO in Eq. (15.42) and $E_T(atom-atom, msp^3.AO)$ in Eq. (15.52) are both $-0.72457\ eV$ per atom corresponding to $-2.89830\ eV$ in total. The energy contribution equivalent to that of a methyl group (Eq. (14.151)) and that of the $C-S$-bond MO of thiols given in the corresponding section matches the energy of the sulfur atom to the $C2sp^3$ HOs.

The symbols of the functional groups of thiophene are given in Table 15.279. The structure of thiophene is shown in Figure 67. The geometrical (Eqs. (15.1-15.5) and (15.42)),

intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of thiophene are given in Tables 15.280, 15.281, and 15.282, respectively. The total energy of thiophene given in Table 15.283 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.282 corresponding to functional-group composition of the molecule. The bond angle parameters of thiophene determined using Eqs. (15.79-15.108) are given in Table 15.284.

Table 15.279. The symbols of functional groups of thiophene.

Functional Group	Group Symbol
$C_a = C_b$ double bond	$C=C$
$C_b - C_b$	$C-C$
$C_a - S - C_a$	$C-S-C$
CH	CH

Table 15.280. The geometrical bond parameters of thiophene and experimental values [1].

Parameter	$C=C$ Group	$C-C$ Group	$C-S-C$ Group	CH Group
a (a_0)	1.45103	1.77965	1.74058	1.53380
c' (a_0)	1.30463	1.33404	1.62766	1.01120
Bond Length $2c'$ $(Å)$	1.38076	1.41188	1.72264	1.07021
Exp. Bond Length $(Å)$	1.370 (thiophene)	1.423 (thiophene)	1.714 (thiophene)	1.078 (thiophene)
b,c (a_0)	0.63517	1.17792	0.61671	1.15326
e	0.89910	0.74961	0.93513	0.65928

Table 15.281. The MO to HO intercept geometrical bond parameters of thiophene. R_1 is an alkyl group and R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom, msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' $(°)$	θ_1 $(°)$	θ_2 $(°)$	d_1 (a_0)	d_2 (a_0)
$C-H$ (C_aH)	C_a	-1.13380	-0.72457	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49326	84.49	95.51	44.74	1.08953	0.07833
$C-H$ (C_bH)	C_b	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	82.21	97.79	43.14	1.11914	0.10794
$C_a=(H)C_b-C_b(H)=C_a$	C_b	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	91.57	88.43	42.49	1.31226	0.02177
$C_a=C_b(H)(H)C_b=C_a$	C_b	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	136.36	43.64	59.86	0.72857	0.57606
$SC_a=C_b(H)$	C_a	-1.13380	-0.72457	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49326	137.14	42.86	60.85	0.70685	0.59777
$C'_aS-C_a=C_b(H)$	C_a	-1.13380	-0.72457	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49326	141.52	38.48	55.36	0.98926	0.63840
$C'_aS-C_a=C_b(H)$	S	-0.72457	-0.72457	0	0		1.3201	0.83600	-16.27490		142.17	37.83	56.24	0.96733	0.66033

Table 15.282. The energy parameters (eV) of functional groups of thiophene.

Parameters	$C=C$ Group	$C-C$ Group	$C-S-C$ Group	CH Group
n_1	2	1	2	1
n_2	0	0	0	0
n_3	0	0	0	0
C_1	0.5	0.5	0.5	0.75
C_2	0.85252	1	0.65700	1
c_1	1	1	1	1
c_2	0.85252	0.85252	0.85252	0.91771
c_3	0	0	0	1
c_4	4	2	4	1
c_5	0	0	0	1
C_{1o}	0.5	0.5	0.5	0.75
C_{2o}	0.85252	1	0.65700	1
V_e (eV)	-104.37986	-33.80733	-96.78916	-39.09538
V_p (eV)	20.85777	10.19898	16.71820	13.45505
T (eV)	35.96751	9.49831	27.80371	12.74462
V_m (eV)	-17.98376	-4.74915	-13.90186	-6.37231
$E(AO/HO)$ (eV)	0	-14.63489	0	-14.63489
$\Delta E_{H_2MO}(AO/HO)$ (eV)	-2.26759	-1.85836	-2.89830	-2.26758
$E_T(AO/HO)$ (eV)	2.26759	-12.77653	2.89830	-12.36731
$E_T(H_2MO)$ (eV)	-63.27075	-31.63572	-63.27080	-31.63533
$E_T\left(atom-atom,msp^3.AO\right)$ (eV)	-2.26759	-2.26759	-2.89830	0
$E_T(MO)$ (eV)	-65.53833	-33.90295	-66.16903	-31.63537
ω $\left(10^{15}\ rad/s\right)$	15.4421	12.3131	10.3184	28.9084
E_K (eV)	10.16428	8.10471	6.79173	19.02803
$\bar{E}_D$ (eV)	-0.20668	-0.19095	-0.17058	-0.27301
$\bar{E}_{Kvib}$ (eV)	0.17897 [6]	0.14829 [48]	0.08146 [41]	0.39427 [56]
$\bar{E}_{osc}$ (eV)	-0.11720	-0.11680	-0.12985	-0.07587
E_{mag} (eV)	0.14803	0.14803	0.14803	0.14803
$E_T(Group)$ (eV)	-65.77272	-34.01976	-66.42873	-31.71124
$E_{initial}(c_4\ AO/HO)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(c_5\ AO/HO)$ (eV)	0	0	0	-13.59844
$E_D(Group)$ (eV)	7.23317	4.74998	7.88917	3.32988

Table 15.283. The total bond energies of thiophene calculated using the functional group composition and the energies of Table 15.282 compared to the experimental values [2].

Formula	Name	$C=C$	$C-C$	$C-S-C$	CH	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_4H_4S	Thiophene	2	1	1	4	40.42501	40.430	0.00013

Table 15.284. The bond angle parameters of thiophene and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.B)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.B)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HC_aS$	2.02241	3.25533	4.6030	-15.55033	3	-10.36001	S	0.87495 Eq. (15.65))	0.76144 (Eq. 15.126))	0.75	0.76144 (Eq. 15.126))	0.75	0.87495	0				119.58	119.9 (thiophene)
$\angle C_bC_aH_a$																119.58	115.84	124.58	
$\angle H_bC_bC_b$	2.02241	2.66807	4.1633	-16.68412 C_b	14	-15.95954 C_b	6	0.81549	0.85252	0.75	1	0.75	1.04540	0				124.58	124.3 (thiophene)
$\angle H_aC_aC_b$	2.02241	2.60925	4.1633	-16.68412 C_a	14	-15.95954 C_b	6	0.81549	0.85252	0.75	1	0.75	1.04540	0				127.57	
$\angle H_bC_bC_a$	2.02241	2.60925	4.0825	-17.09334 C_b	18	-16.68412 C_a	14	0.79597	0.81549	0.75	1	0.75	1.02453	0				123.13	
$\angle C_bC_bH_b$																123.13	113.60	123.27	124.3 (thiophene)
$\angle C_bC_aS$	2.60925	3.25533	4.9809	-17.81791 C_b	27	-10.36001	S	0.76360	0.65700 Eq. (15.153))	1	0.65700 Eq. (15.153))	1	0.71030	-0.72457				115.84	115.5 (thiophene)
$\angle C_aSC_a$	3.25533	3.25533	4.7958	-16.68412	14	-16.68412	14	0.81549	0.81549	1	1	1	0.81549	-1.85836				94.89	92.2 (thiophene)
$\angle C_aC_bC_b$	2.60925	2.66807	4.4159	-16.88873	15	-18.02252	29	0.80561	0.75493	1	1	1	0.78027	-1.85836				113.60	112.5 (thiophene)

IMIDAZOLE

Imidazole having the formula $C_3H_4N_2$ comprises a conjugated system that is equivalent to pyrrole with one of the conjugated CH groups replaced by a nitrogen atom. The CH, NH, and $C=C$ groups are equivalent to the corresponding groups of pyrrole, furan, and thiophene where present. In addition, the nitrogen substitution creates a $C-N=C$ moiety comprising $C-N$ and $N=C$ functional groups. The $C-N$ bonding is the same as that of a tertiary amine except that the hybridization term c_2 in Eqs. (15.42) and (15.52) is that of the amino group of aniline, $c_2(arylC2sp^3HO\ to\ N)=0.84665$ (Eq. (15.152)). The hybridization factor provides double-bond character to match the group to the other orbitals of the molecule. $\Delta E_{H_2MO}(AO/HO)$ in Eq. (15.42) and $E_T(atom-atom,msp^3.AO)$ in Eq. (15.52) are both $-0.92918\ eV$ (Eq. (14.513)). This matches the energy of the group to that of the contiguous $N=C$ group wherein $\Delta E_{H_2MO}(AO/HO)$ in Eq. (15.42) and $E_T(atom-atom,msp^3.AO)$ in Eq. (15.52) are both $-0.92918\ eV$ (Eq. (14.513)) per atom of the double bond with aromatic character as in the case of the prior heterocyclic compounds. As in the prior cases of pyrrole, furan, and thiophene, $n_1=2$ and C_2 and C_{2o} are the same as $C_2(benzeneC2sp^3HO)=0.85252$ (Eq. (15.143)) in Eqs. (15.42) and (15.52). To match the energy of the nitrogen to the $C2sp^3$ HO, c_2 of the $N=C$-bond MO is also given by Eq. (15.152). These parameters also provide an energy match to the $C-N-C$ group.

As in the case of pyrrole, the $C-N-C$-bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with $n_1=2$ in Eqs. (15.42) and (15.52). The hybridization factor $c_2(arylC2sp^3HO\ to\ N)=0.84665$ (Eq. (15.152)) matches the double-bond character of the $C2sp^3$ HOs to the N atom of the NH group, and C_2 and C_{2o} in Eqs. (15.42) and (15.52) become that of benzene given by Eq. (15.143), $C_2(benzeneC2sp^3HO)=0.85252$. Furthermore, $\Delta E_{H_2MO}(AO/HO)$ in Eq. (15.42) and $E_T(atom-atom,msp^3.AO)$ in Eq. (15.52) are both $-0.92918\ eV$ (Eq. (14.513)) per atom corresponding to $-3.71673\ eV$ in total.

The symbols of the functional groups of imidazole are given in Table 15.285. The structure of imidazole is shown in Figure 68. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of imidazole are given in Tables 15.286, 15.287, and 15.288, respectively. The total energy of imidazole given in Table 15.289 was calculated as the sum over the integer multiple of each $E_D(_{Group})$ of Table 15.288 corresponding to functional-group composition of the molecule. The bond angle parameters of imidazole determined using Eqs. (15.79-15.108) are given in Table 15.290.

Table 15.285. The symbols of functional groups of imidazole.

Functional Group	Group Symbol
$C_a = C_b$ double bond	$C = C$
$N_b = C_c$ double bond	$N = C$
$C_b - N_b$	$C - N$
$C_a - N_a - C_c$	$C - N - C$
N_aH group	NH
CH	CH

Table 15.286. The geometrical bond parameters of imidazole and experimental values [1].

Parameter	$C=C$ Group	$N=C$ Group	$C-N$ Group	$C-N-C$ Group	NH Group	CH Group
$a\ (a_0)$	1.45103	1.44926	1.82450	1.43222	1.24428	1.53380
$c'\ (a_0)$	1.30463	1.30383	1.35074	1.29614	0.94134	1.01120
Bond Length $2c'$ ($\AA$)	1.38076	1.37991	1.42956	1.37178	0.996270	1.07021
Exp. Bond Length ($\AA$)	1.382 (pyrrole)			1.370 (pyrrole)	0.996 (pyrrole)	1.076 (pyrrole)
$b,c\ (a_0)$	0.63517	0.63276	1.22650	0.60931	0.81370	1.15326
e	0.89910	0.89965	0.74033	0.90499	0.75653	0.65928

Table 15.287. The MO to HO intercept geometrical bond parameters of imidazole. R_1 is an alkyl group and R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C-H\ (C_aH)$	C_a	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	83.35	96.65	43.94	1.10452	0.09331
$C-H\ (C_bH)$	C_b	-1.13380	-0.46459	0	0	-153.21408	0.91771	0.82840	-16.42414	-16.23327	85.93	94.07	45.77	1.06995	0.05875
$C-H\ (C_cH)$	C_c	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	84.49	95.51	44.47	1.08953	0.07833
$C_a=(H)C_b-N_b=C_c$	C_b	-0.46459	-1.13380	0	0	-153.21408	0.91771	0.82840	-16.42414	-16.23327	90.36	89.64	42.49	1.34547	0.00527
$C_a=(H)C_b-N_b=C_c$	N_b	-0.46459	-0.92918	0	0		0.93084	0.83885	-16.21953		91.32	88.68	43.14	1.33135	0.01939
$C_a=C_b(H)N_b=C_c$	C_b	-1.13380	-0.46459	0	0	-153.21408	0.91771	0.82840	-16.42414	-16.23327	137.64	42.36	61.49	0.69250	0.61213
$HN_aC_a=C_b(H)$	C_a	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	136.75	43.25	60.35	0.71784	0.58678
$C_c(H)N_a-C_a=C_b(H)$	C_a	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	138.54	41.46	61.09	0.69238	0.60376
$C_c(H)N_a-C_a=C_b(H)$	N_a	-0.92918	-0.92918	0	0		0.93084	0.81549	-16.68411		138.92	41.08	61.59	0.68147	0.61467
$N-H\ (N_aH)$	N_a	-0.92918	-0.92918	0	0		0.93084	0.81549	-16.68411		117.34	62.66	62.90	0.56678	0.37456
$(H)C_c-N_aC_a=C_b(H)$	C_c	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	138.92	41.08	61.59	0.68147	0.61467
$C_a=(H)C_bN_b=C_c$	C_c	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	137.31	42.69	60.92	0.70446	0.59938
$C_a=(H)C_bN_b=C_c$	N_b	-0.92918	-0.46459	0	0		0.93084	0.83885	-16.21953		138.20	41.80	62.08	0.67849	0.62534

Table 15.288. The energy parameters (eV) of functional groups of imidazole.

Parameters	$C=C$ Group	$N=C$ Group	$C-N$ Group	$C-N-C$ Group	NH Group	CH Group
n_1	2	2	1	2	1	1
n_2	0	0	0	0	0	0
n_3	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.5	0.75	0.75
C_2	0.85252	0.85252	1	0.85252	0.93613	1
c_1	1	1	1	1	0.75	1
c_2	0.85252	0.84665	0.84665	0.84665	0.92171	0.91771
c_3	0	0	0	0	1	1
c_4	4	4	2	4	1	1
c_5	0	0	0	0	1	1
C_{1o}	0.5	0.5	0.5	0.5	0.75	0.75
C_{2o}	0.85252	0.85252	1	0.85252	1	1
V_e (eV)	-104.37986	-103.92756	-32.44864	-106.58684	-39.48897	-39.09538
V_p (eV)	20.85777	20.87050	10.07285	20.99432	14.45367	13.45505
T (eV)	35.96751	35.85539	8.89248	37.21047	15.86820	12.74462
V_m (eV)	-17.98376	-17.92770	-4.44624	-18.60523	-7.93410	-6.37231
$E(_{AO/HO})$ (eV)	0	0	-14.63489	0	-14.53414	-14.63489
$\Delta E_{H_2MO}(_{AO/HO})$ (eV)	-2.26759	-1.85836	-0.92918	-3.71673	0	-2.26758
$E_T(_{AO/HO})$ (eV)	2.26759	1.85836	-13.70571	3.71673	-14.53414	-12.36731
$E_T(_{H_2MO})$ (eV)	-63.27075	-63.27100	-31.63527	-63.27056	-31.63534	-31.63533
$E_T(atom-atom, msp^3.AO)$ (eV)	-2.26759	-1.85836	-0.92918	-3.71673	0	0
$E_T(_{MO})$ (eV)	-65.53833	-65.12910	-32.56455	-66.98746	-31.63537	-31.63537
ω $(10^{15}\ rad/s)$	15.4421	15.4704	21.5213	15.7474	48.7771	28.9084
E_K (eV)	10.16428	10.18290	14.16571	10.36521	32.10594	19.02803
$\bar{E}_D$ (eV)	-0.20668	-0.20558	-0.24248	-0.21333	-0.35462	-0.27301
$\bar{E}_{Kvib}$ (eV)	0.17897 [6]	0.20768 [58]	0.12944 [23]	0.11159 [12]	0.40696 [24]	0.39427 [56]
$\bar{E}_{osc}$ (eV)	-0.11720	-0.10174	-0.17775	-0.15754	-0.15115	-0.07587
E_{mag} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(_{Group})$ (eV)	-65.77272	-65.33259	-32.74230	-67.30254	-31.78651	-31.71124
$E_{initial}(c_4\ _{AO/HO})$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.53414	-14.63489
$E_{initial}(c_5\ _{AO/HO})$ (eV)	0	0	0	0	-13.59844	-13.59844
$E_D(_{Group})$ (eV)	7.23317	6.79303	3.47253	8.76298	3.51208	3.32988

Table 15.289. The total bond energies of imidazole calculated using the functional group composition and the energies of Table 15.288 compared to the experimental values [2].

Formula	Name	$C=C$	$N=C$	$C'-N$	$C'-N-C'$	NH	CH	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_3H_4N_2$	Imidazole	1	1	1	1	1	3	39.76343	39.74106	-0.00056

Table 15.290. The bond angle parameters of imidazole and experimental values [59]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3B)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3B)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HC'_aN_a$	2.02241	2.59228	4.0166	-14.82575	1	-14.53414	N	0.91771	0.92171 Eq. (15.151))	0.75	1	0.75	1.00435	0				120.51	117.4 (imidazole)
$\angle C'_bC'_aH_a$																120.51	106.63	132.86	136.3 (imidazole)
$\angle HN_aC'_a$	1.88268	2.59228	3.8987	-14.53414	N	-16.49325	13	0.84665 (Eq. (15.151))	0.82493 (Eq. (15.64))	0.75	1	0.75	0.97435	0				120.37	122.9 (imidazole)
$\angle H_aC'_aC'_b$	2.02241	2.60925	4.2895	-16.88873 C'_a	15	-15.75493 C'_b	4	0.80561	0.86359	0.75	1	0.75	1.07196	0				135.30	136.3 (imidazole)
$\angle H_bC'_bC'_a$	2.02241	2.60925	4.2740	-15.95954 C'_b	6	-14.82575 C'_a	1	0.85252	0.91771	0.75	1	0.75	1.07647	0				134.28	133.2 (imidazole)
$\angle N_bC'_bH_b$																134.28	111.18	114.54	115.8 (imidazole)
$\angle H_cC'_cN_a$	2.02241	2.59228	3.8471	-15.95954 C'_c	6	-14.53414	N	0.87495	0.84665 (Eq. (15.152))	0.75	1	0.75	0.96765					112.37	110.4 (imidazole)
$\angle N_bC'_cH_c$																112.37	109.83	137.80	138.2 (imidazole)
$\angle HN_aC'_c$	1.88268	2.59228	4.0661	-14.53414	N	-15.76868	6	0.84665 (Eq. (15.151))	0.86284 (Eq. (15.64))	0.75	1	0.75	1.01912	0				129.96	129.1 (imidazole)
$\angle N_aC'_aC'_b$	2.59228	2.60925	4.1952	-14.53414	N	-17.09334 C'_b	18	0.84665 (Eq. (15.152))	0.79597	1	1	1	0.82131	-1.44915				107.52	106.3 (imidazole)
$\angle C'_aN_aC'_c$	2.59228	2.59228	4.2426	-17.81791	26	-17.81791	26	0.76360	0.76360	1	1	1	0.76360	-1.85836				109.83	107.2 (imidazole)
$\angle C'_cN_bC'_b$	2.60766	2.70148	4.3128	-17.61330	23	-17.61330	25	0.77247	0.77247	1	1	1	0.77247	-1.85836				108.64	105.4 (imidazole)
$\angle C'_aC'_bN_b$	2.60925	2.70148	4.3818	-15.95955	6	-14.53414	N	0.85252	0.84665 (Eq. (15.152))	1	1	1	0.84958	-1.85836				111.18	109.8 (imidazole)
$\angle N_aC'_cN_b$	2.59228	2.60766	4.2544	-16.68411	13	-16.21953	8	0.81549	0.83885	1	1	1	0.82717	-1.44915				109.80	111.3 (imidazole)

PYRIDINE

Pyridine has the formula C_5H_5N and comprises the benzene molecule with one CH group replaced by a nitrogen atom which gives rise to a $C\overset{3e}{=}N$ functional group. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups are equivalent to those of benzene given in the Aromatic and Heterocyclic Compounds section with the aromaticity maintained by the electrons from nitrogen in the $C\overset{3e}{=}N$ group which is also aromatic.

As in the case of the aromatic carbons of benzene, each pyridine $C2sp^3$ HO initially has four unpaired electrons. Each $C-H$ bond has two paired electrons with one donated from the H AO and the other from the $C2sp^3$ HO. In pyridine the three $N2p$ electrons are donated to the aromatic bond. Thus, as in the case of the $C\overset{3e}{=}C$ group, each $C\overset{3e}{=}N$ bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from the $C2sp^3$ HO and the $N2p$ AO of the participating carbon and nitrogen atoms, respectively.

The solution of the $C\overset{3e}{=}N$ functional group comprises the hybridization of the $2s$ and $2p$ AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the nitrogen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. The $C\overset{3e}{=}N$-bond MO is solved as a double bond with $n_1=2$ in Eqs. (15.42) and (15.147). The hybridization factor $c_2(C2sp^3HO\ to\ N)=0.91140$ (Eq. (15.116)) matches the double-bond character of the $C2sp^3$ HO to the N atom, and C_2 and C_{2o} in Eqs. (15.42) and (15.147) are also given by Eq. (15.116) in order to match the nitrogen to the aromatic $C2sp^3$ HO such that $\Delta E_{H_2MO}(AO/HO)=0$ in Eq. (15.42). Furthermore, $E_T(atom-atom,msp^3.AO)$ of the $C\overset{3e}{=}N$-bond MO in Eq. (15.147) due to the charge donation from the C and N atoms to the MO is $-1.44915\ eV$ corresponding to an energy contribution from each atom that is equivalent to that of an independent methyl group, $-0.72457\ eV$ (Eq. (14.151)). The contributions are also the same as those for a primary amine group as given in the corresponding section. As in the case of benzene, the aromatic $E_T(Group)$ and $E_D(Group)$ are

given by Eqs. (15.146) and (15.147), respectively, with $f_1 = 0.75$. The breakage of the CNC bonds results in three unpaired electrons on the N atom. Thus, the corresponding E_{mag} given by Eq. (15.60) was normalized for the two bonds per atom and for $f_1 = 0.75$ and was subtracted from the total energy of the $C\overset{3e}{=}N$-bond MO in Eq. (15.147). The pyridine vibrational energies are similar to those of benzene [60]; thus, the value for benzene was used.

The symbols of the functional groups of pyridine are given in Table 15.291. The corresponding designation of the structure is shown in Figure 69. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of pyridine are given in Tables 15.292, 15.293, and 15.294, respectively. The total energy of pyridine given in Table 15.295 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.294 corresponding to functional-group composition of the molecule. The bond angle parameters of pyridine determined using Eqs. (15.79-15.108) are given in Table 15.296.

Table 15.291. The symbols of functional groups of pyridine.

Functional Group	Group Symbol
CC (aromatic bond)	$C\overset{3e}{=}C$
CH (aromatic)	CH
$C_a\overset{3e}{=}N$	$C\overset{3e}{=}N$

Table 15.292. The geometrical bond parameters of pyridine and experimental values [1].

Parameter	$C\overset{3e}{=}C$ Group	CH Group	$C\overset{3e}{=}N$ Group
$a\ (a_0)$	1.47348	1.60061	1.47169
$c'\ (a_0)$	1.31468	1.03299	1.27073
Bond Length $2c'$ $(\mathring{A})$	1.39140	1.09327	1.34489
Exp. Bond Length $(\mathring{A})$	1.394 (pyridine)	1.084 (pyridine)	1.340 (pyridine)
$b,c\ (a_0)$	0.66540	1.22265	0.74237
e	0.89223	0.64537	0.86345

Table 15.293. The MO to HO intercept geometrical bond parameters of pyridine. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' $(°)$	θ_1 $(°)$	θ_2 $(°)$	d_1 (a_0)	d_2 (a_0)
$C'-H\ (C'_aH)$	C'_a	-0.54343	-0.85035	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	76.35	103.65	40.11	1.22423	0.19124
$C'-H\ (C'_bH)$	C'_b	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$(H)C'_b(H)C'_a\overset{3e}{=}NC'_a$	C'_a	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	128.54	51.46	58.65	0.76572	0.50501
$(H)C'_b(H)C'_a\overset{3e}{=}NC'_a$	N	-0.54343	-0.54343	0	0		0.93084	0.85503	-15.91261		130.61	49.39	60.97	0.71418	0.55656
$(H)C'_b\overset{3e}{=}C'_a(H)N$	C'_a	-0.54343	-0.85035	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	134.85	45.15	59.72	0.74304	0.57165
$(H)C'_b\overset{3e}{=}C'_a(H)N$ $(H)C'_b\overset{3e}{=}C'_b(H)C'_a(H)$	C'_b	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533

Table 15.294. The energy parameters (eV) of functional groups of pyridine.

Parameters	$\overset{3e}{C=C}$ Group	CH Group	$\overset{3e}{C=N}$ Group
f_1	0.75	1	0.75
n_1	2	1	2
n_2	0	0	0
n_3	0	0	0
C_1	0.5	0.75	0.5
C_2	0.85252	1	0.91140
c_1	1	1	1
c_2	0.85252	0.91771	0.91140
c_3	0	1	0
c_4	3	1	3
c_5	0	1	0
C_{1o}	0.5	0.75	0.5
C_{2o}	0.85252	1	0.91140
$V_e\ (eV)$	-101.12679	-37.10024	-102.01431
$V_p\ (eV)$	20.69825	13.17125	21.41410
$T\ (eV)$	34.31559	11.58941	34.65890
$V_m\ (eV)$	-17.15779	-5.79470	-17.32945
$E(_{AO/HO})\ (eV)$	0	-14.63489	0
$\Delta E_{H_2MO}(_{AO/HO})\ (eV)$	0	-1.13379	0
$E_T(_{AO/HO})\ (eV)$	0	-13.50110	0
$E_T(_{H_2MO})\ (eV)$	-63.27075	-31.63539	-63.27076
$E_T\left(atom-atom,msp^3.AO\right)\ (eV)$	-2.26759	-0.56690	-1.44915
$E_T(_{MO})\ (eV)$	-65.53833	-32.20226	-64.71988
$\omega\ \left(10^{15}\ rad/s\right)$	49.7272	26.4826	43.6311
$E_K\ (eV)$	32.73133	17.43132	28.71875
$\bar{E}_D\ (eV)$	-0.35806	-0.26130	-0.33540
$\bar{E}_{Kvib}\ (eV)$	0.19649 [49]	0.35532 Eq. (13.458)	0.19649 [49]
$\bar{E}_{osc}\ (eV)$	-0.25982	-0.08364	-0.23715
$E_{mag}\ (eV)$	0.14803	0.14803	0.09457
$E_T(_{Group})\ (eV)$	-49.54347	-32.28590	-48.82472
$E_{initial}(_{c_4\ AO/HO})\ (eV)$	-14.63489	-14.63489	-14.63489
$E_{initial}(_{c_5\ AO/HO})\ (eV)$	0	-13.59844	0
$E_D(_{Group})\ (eV)$	5.63881	3.90454	4.92005

Table 15.295. The total bond energies of pyridine calculated using the functional group composition and the energies of Table 15.294 compared to the experimental values [2].].

Formula	Name	$\overset{3e}{C=C}$	CH	$\overset{3e}{C=N}$ Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_5H_5N	Pyridine	4	5	2	51.91802	51.87927	-0.00075

Table 15.296. The bond angle parameters of pyridine and experimental values [1]. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3B)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3B)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CCC$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	20	-17.17218	20	0.79232	0.79232	1	1	1	0.79232	-1.85836				120.19	120 [50-52] (benzene) 118.3 (pyridine) 118.5 (pyridine)
$\angle CCH$ (aromatic)																120.19		119.91	120 [50-52] (benzene) 121.3 (pyridine)
$\angle HC_aN$	2.06598	2.54147	3.9497	-14.82575	1	-14.53414	N	0.91771	0.91140 Eq. (15.116))	0.75	1	0.75	0.99312	0				117.65	115.9 (pyridine)
$\angle NC_aC_b$	2.54147	2.62936	4.5607	-14.53414	N	-16.52644 C_b	12	0.91140 Eq. (15.116))	0.82327	1	1	1	0.86734	-1.44915				123.76	123.9 (pyridine)
$\angle C_aNC_a$	2.54147	2.54147	4.3359	-17.71560	24	-17.71560	24	0.76801	0.76801	1	1	1	0.76801	-1.85836				117.09	116.8 (pyridine)

PYRIMIDINE

Pyrimidine has the formula $C_4H_4N_2$ and comprises the pyridine molecule with one additional CH group replaced by a nitrogen atom which gives rise to a second $C\overset{3e}{=}N$ functional group that is equivalent to that of pyridine given in the corresponding section. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups are also equivalent to those of pyridine and benzene given in the Aromatic and Heterocyclic Compounds section with the aromaticity maintained by the electrons from nitrogen in the $C\overset{3e}{=}N$ group which is also aromatic.

The symbols of the functional groups of pyrimidine are given in Table 15.297. The corresponding designation of the structure is shown in Figure 70. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of pyrimidine are given in Tables 15.298, 15.299, and 15.300, respectively. The total energy of pyrimidine given in Table 15.301 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.300 corresponding to functional-group composition of the molecule. The bond angle parameters of pyrimidine determined using Eqs. (15.79-15.108) are given in Table 15.302.

Table 15.297. The symbols of functional groups of pyrimidine.

Functional Group	Group Symbol
CC (aromatic bond)	$C\overset{3e}{=}C$
CH (aromatic)	CH
$C_{a,b,d}\overset{3e}{=}N$	$C\overset{3e}{=}N$

Table 15.298. The geometrical bond parameters of pyrimidine and experimental values [1].

Parameter	$C\overset{3e}{=}C$ Group	CH Group	$C\overset{3e}{=}N$ Group
a (a_0)	1.47348	1.60061	1.47169
c' (a_0)	1.31468	1.03299	1.27073
Bond Length $2c'$ $(Å)$	1.39140	1.09327	1.34489
Exp. Bond Length $(Å)$	1.393 (pyrimidine)	1.084 (pyridine)	1.340 (pyrimidine)
b,c (a_0)	0.66540	1.22265	0.74237
e	0.89223	0.64537	0.86345

Table 15.299. The MO to HO intercept geometrical bond parameters of pyrimidine. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' $(°)$	θ_1 $(°)$	θ_2 $(°)$	d_1 (a_0)	d_2 (a_0)
$C'-H\ (C'_aH)$	C'_a	-0.54343	-0.54343	-0.56690	0	-153.26945	0.91771	0.82562	-16.47951	-16.28864	78.27	101.73	41.39	1.20084	0.16785
$C'-H\ (C'_{b,d}H)$	C'_b C'_d	-0.54343	-0.85035	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	76.35	103.65	40.11	1.22423	0.19124
$C'-H\ (C'_cH)$	C'_c	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$(H)C'_c(H)C'_b\overset{3e}{=}N_bC'_a$ $(H)C'_c(H)C'_d\overset{3e}{=}N_aC'_a$	C'_b C'_d	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	128.54	51.46	58.65	0.76572	0.50501
$(H)C'_c(H)C'_b\overset{3e}{=}N_bC'_a$ $(H)C'_c(H)C'_d\overset{3e}{=}N_aC'_a$	N_b N_a	-0.54343	-0.54343	0	0		0.93084	0.85503	-15.91261		130.61	49.39	60.97	0.71418	0.55656
$(H)C'_c(H)C'_bN_b\overset{3e}{=}C'_a(H)$ $(H)C'_c(H)C'_dN_a\overset{3e}{=}C'_a(H)$	C'_a	-0.54343	-0.54343	-0.56690	0	-153.26945	0.91771	0.82562	-16.47951	-16.28865	129.26	50.74	59.44	0.74824	0.52249
$(H)C'_c(H)C'_bN_b\overset{3e}{=}C'_a(H)$ $(H)C'_c(H)C'_dN_a\overset{3e}{=}C'_a(H)$	N_b N_a	-0.54343	-0.54343	0	0		0.93084	0.85503	-15.91261		130.61	49.39	60.97	0.71418	0.55656
$N_a(H)C'_d\overset{3e}{=}C'_c(H)C'_b$ $N_b(H)C'_b\overset{3e}{=}C'_c(H)C'_d$	C'_c	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533
$N_a(H)C'_d\overset{3e}{=}C'_c(H)C'_b$ $N_b(H)C'_b\overset{3e}{=}C'_c(H)C'_d$	C'_b C'_d	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	134.85	45.15	59.72	0.74304	0.57165

Table 15.300. The energy parameters (eV) of functional groups of pyrimidine.

Parameters	$\overset{3e}{C=C}$ Group	CH Group	$\overset{3e}{C=N}$ Group
f_1	0.75	1	0.75
n_1	2	1	2
n_2	0	0	0
n_3	0	0	0
C_1	0.5	0.75	0.5
C_2	0.85252	1	0.91140
c_1	1	1	1
c_2	0.85252	0.91771	0.91140
c_3	0	1	0
c_4	3	1	3
c_5	0	1	0
C_{1o}	0.5	0.75	0.5
C_{2o}	0.85252	1	0.91140
$V_e\ (eV)$	-101.12679	-37.10024	-102.01431
$V_p\ (eV)$	20.69825	13.17125	21.41410
$T\ (eV)$	34.31559	11.58941	34.65890
$V_m\ (eV)$	-17.15779	-5.79470	-17.32945
$E(AO/HO)\ (eV)$	0	-14.63489	0
$\Delta E_{H_2MO}(AO/HO)\ (eV)$	0	-1.13379	0
$E_T(AO/HO)\ (eV)$	0	-13.50110	0
$E_T(H_2MO)\ (eV)$	-63.27075	-31.63539	-63.27076
$E_T\left(atom-atom,msp^3.AO\right)\ (eV)$	-2.26759	-0.56690	-1.44915
$E_T(MO)\ (eV)$	-65.53833	-32.20226	-64.71988
$\omega\ \left(10^{15}\ rad/s\right)$	49.7272	26.4826	43.6311
$E_K\ (eV)$	32.73133	17.43132	28.71875
$\bar{E}_D\ (eV)$	-0.35806	-0.26130	-0.33540
$\bar{E}_{Kvib}\ (eV)$	0.19649 [49]	0.35532 Eq. (13.458)	0.19649 [49]
$\bar{E}_{osc}\ (eV)$	-0.25982	-0.08364	-0.23715
$E_{mag}\ (eV)$	0.14803	0.14803	0.09457
$E_T(Group)\ (eV)$	-49.54347	-32.28590	-48.82472
$E_{initial}(c_4\ AO/HO)\ (eV)$	-14.63489	-14.63489	-14.63489
$E_{initial}(c_5\ AO/HO)\ (eV)$	0	-13.59844	0
$E_D(Group)\ (eV)$	5.63881	3.90454	4.92005

Table 15.301. The total bond energies of pyrimidine calculated using the functional group composition and the energies of Table 15.300 compared to the experimental values [2].].

Formula	Name	$\overset{3e}{C=C}$	CH	$\overset{3e}{C=N}$ Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_4H_4N_2$	Pyrimidine	2	4	4	46.57597	46.51794	-0.00125

Table 15.302. The bond angle parameters of pyrimidine and experimental values [1]. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3B)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3B)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CCC$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	20	-17.17218	20	0.79232	0.79232	1	1	1	0.79232	-1.85836				120.19	120 [50-52] (benzene) 118.3 (pyridine) 118.5 (pyridine)
$\angle CCH$ (aromatic)																120.19		119.91	120 [50-52] (benzene) 121.3 (pyridine)
$\angle HCN$	2.06598	2.54147	3.9497	-14.82575	1	-14.53414	N	0.91771	0.91140 Eq. (15.116))	0.75	1	0.75	0.99312	0				117.65	115.9 (pyridine)
$\angle NCC$	2.54147	2.62936	4.5607	-14.53414	N	-16.52644	13	0.91140 Eq. (15.116))	0.82327	1	1	1	0.86734	-1.44915				123.76	123.9 (pyridine)
$\angle CNC$	2.54147	2.54147	4.3359	-17.71560	24	-17.71560	24	0.76801	0.76801	1	1	1	0.76801	-1.85836				117.09	115.5 (pyrimidine)
$\angle NCN$	2.54147	2.54147	4.5826	-15.55033	3	-15.55033	3	0.87495	0.87495	1	1	1	0.87495	-1.85836				128.73	127.6 (pyrimidine)

PYRAZINE

Pyrazine has the formula $C_4H_4N_2$ and comprises the pyrimidine molecule with para rather than ortho aromatic nitrogen atoms. The $C\overset{3e}{=}N$ functional group is equivalent to that of pyrimidine and pyridine given in the corresponding sections. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups are also equivalent to those of pyrimidine, pyridine, and benzene given in the Aromatic and Heterocyclic Compounds section with the aromaticity maintained by the electrons from nitrogen in the $C\overset{3e}{=}N$ group which is also aromatic.

The symbols of the functional groups of pyrazine are given in Table 15.303. The corresponding designation of the structure is shown in Figure 71. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of pyrazine are given in Tables 15.304, 15.305, and 15.306, respectively. The total energy of pyrazine given in Table 15.307 was calculated as the sum over the integer multiple of each $E_D(_{Group})$ of Table 15.306 corresponding to functional-group composition of the molecule. The bond angle parameters of pyrazine determined using Eqs. (15.79-15.108) are given in Table 15.308.

Table 15.303. The symbols of functional groups of pyrazine.

Functional Group	Group Symbol
CC (aromatic bond)	$C\overset{3e}{=}C$
CH (aromatic)	CH
$C_a\overset{3e}{=}N$	$C\overset{3e}{=}N$

Table 15.304. The geometrical bond parameters of pyrazine and experimental values [1].

Parameter	$\overset{3e}{C=C}$ Group	CH Group	$\overset{3e}{C=N}$ Group
$a\ (a_0)$	1.47348	1.60061	1.47169
$c'\ (a_0)$	1.31468	1.03299	1.27073
Bond Length $2c'$ ($\AA$)	1.39140	1.09327	1.34489
Exp. Bond Length ($\AA$)	1.339 (pyrazine)	1.115 (pyrazine)	1.403 (pyrazine)
$b,c\ (a_0)$	0.66540	1.22265	0.74237
e	0.89223	0.64537	0.86345

Table 15.305. The MO to HO intercept geometrical bond parameters of pyrazine. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C-H\ (C_aH)$	C_a	-0.54343	-0.85035	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	76.35	103.65	40.11	1.22423	0.19124
$(H)C_a(H)C_a\overset{3e}{=}NC_a$	C_a	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	128.54	51.46	58.65	0.76572	0.50501
$(H)C_a(H)C_a\overset{3e}{=}NC_a$	N	-0.54343	-0.54343	0	0		0.93084	0.85503	-15.91261		130.61	49.39	60.97	0.71418	0.55656
$N(H)C_a\overset{3e}{=}C_a(H)N$	C_a	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	134.85	45.15	59.72	0.74304	0.57165

Table 15.306. The energy parameters (eV) of functional groups of pyrazine.

Parameters	$C\overset{3e}{=}C$ Group	CH Group	$C\overset{3e}{=}N$ Group
f_1	0.75	1	0.75
n_1	2	1	2
n_2	0	0	0
n_3	0	0	0
C_1	0.5	0.75	0.5
C_2	0.85252	1	0.91140
c_1	1	1	1
c_2	0.85252	0.91771	0.91140
c_3	0	1	0
c_4	3	1	3
c_5	0	1	0
C_{1o}	0.5	0.75	0.5
C_{2o}	0.85252	1	0.91140
$V_e\ (eV)$	-101.12679	-37.10024	-102.01431
$V_p\ (eV)$	20.69825	13.17125	21.41410
$T\ (eV)$	34.31559	11.58941	34.65890
$V_m\ (eV)$	-17.15779	-5.79470	-17.32945
$E(AO/HO)\ (eV)$	0	-14.63489	0
$\Delta E_{H_2MO}(AO/HO)\ (eV)$	0	-1.13379	0
$E_T(AO/HO)\ (eV)$	0	-13.50110	0
$E_T(H_2MO)\ (eV)$	-63.27075	-31.63539	-63.27076
$E_T(atom-atom,msp^3.AO)\ (eV)$	-2.26759	-0.56690	-1.44915
$E_T(MO)\ (eV)$	-65.53833	-32.20226	-64.71988
$\omega\ (10^{15}\ rad/s)$	49.7272	26.4826	43.6311
$E_K\ (eV)$	32.73133	17.43132	28.71875
$\bar{E}_D\ (eV)$	-0.35806	-0.26130	-0.33540
$\bar{E}_{Kvib}\ (eV)$	0.19649 [49]	0.35532 Eq. (13.458)	0.19649 [49]
$\bar{E}_{osc}\ (eV)$	-0.25982	-0.08364	-0.23715
$E_{mag}\ (eV)$	0.14803	0.14803	0.09457
$E_T(Group)\ (eV)$	-49.54347	-32.28590	-48.82472
$E_{initial}(c_4\ AO/HO)\ (eV)$	-14.63489	-14.63489	-14.63489
$E_{initial}(c_5\ AO/HO)\ (eV)$	0	-13.59844	0
$E_D(Group)\ (eV)$	5.63881	3.90454	4.92005

Table 15.307. The total bond energies of pyrazine calculated using the functional group composition and the energies of Table 15.306 compared to the experimental values [2].`].

Formula	Name	$\overset{3e}{C=C}$	CH	$\overset{3e}{C=N}$ Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_4H_4N_2$	Pyrazine	2	4	4	46.57597	46.51380	0.00095

Table 15.308. The bond angle parameters of pyrazine and experimental values [1]. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3B)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3B)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CCC$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	20	-17.17218	20	0.79232	0.79232	1	1	1	0.79232	-1.85836				120.19	120 [50-52] (benzene) 118.3 (pyridine) 118.5 (pyridine)
$\angle CCH$ (aromatic)																120.19		119.91	120 [50-52] (benzene) 121.3 (pyridine)
$\angle HCN$	2.06598	2.54147	3.9497	-14.82575	1	-14.53414	N	0.91771	0.91140 Eq. (15.116))	0.75	1	0.75	0.99312	0				117.65	115.9 (pyridine)
$\angle CCH$																117.65	116.81	125.54	123.9 (pyrazine)
$\angle NCC$	2.54147	2.62936	4.4045	-14.53414	N	-17.09334	7	0.91140 Eq. (15.116))	0.79597	1	1	1	0.85368	-1.44915				116.81	115.6 (pyrazine
$\angle CNC$	2.54147	2.54147	4.3359	-17.71560	24	-17.71560	24	0.76801	0.76801	1	1	1	0.76801	-1.85836				117.09	116.8 (pyrimidine)

QUINOLINE

Quinoline has the formula C_9H_7N and comprises the naphthalene molecule with one CH group replaced by a nitrogen atom which gives rise to a $C\overset{3e}{=}N$ functional group. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups are equivalent to those of naphthalene given in the corresponding section with the aromaticity maintained by the electrons from nitrogen in the $C\overset{3e}{=}N$ group which is also aromatic. The $C-C$ functional group is also equivalent to that of naphthalene. The bonding in quinoline can be further considered as a linear combination of the naphthalene and pyridine groups wherein the $C\overset{3e}{=}N$ group is equivalent to that of pyridine, pyrimidine, and pyrazine as given in the corresponding sections.

The symbols of the functional groups of quinoline are given in Table 15.309. The corresponding designation of the structure is shown in Figure 72. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of quinoline are given in Tables 15.310, 15.311, and 15.312, respectively. The total energy of quinoline given in Table 15.313 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.312 corresponding to functional-group composition of the molecule. The bond angle parameters of quinoline determined using Eqs. (15.79-15.108) are given in Table 15.314.

Table 15.309. The symbols of functional groups of quinoline.

Functional Group	Group Symbol
CC (aromatic bond)	$C\overset{3e}{=}C$
CH (aromatic)	CH
C_b-C_b (bridging bond)	$C-C$
$C_{a,d}\overset{3e}{=}N$	$C\overset{3e}{=}N$

Table 15.310. The geometrical bond parameters of quinoline and experimental values [1].

Parameter	$\overset{3e}{C=C}$ Group	CH Group	$C-C$ Group	$\overset{3e}{C=N}$ Group
$a\ (a_0)$	1.47348	1.60061	1.75607	1.47169
$c'\ (a_0)$	1.31468	1.03299	1.32517	1.27073
Bond Length $2c'$ $(\AA)$	1.39140	1.09327	1.40250	1.34489
Exp. Bond Length $(\AA)$	1.40 (avg.) (naphthalene)	1.101 (benzene)	1.42 (naphthalene)	1.340 (pyridine)
$b,c\ (a_0)$	0.66540	1.22265	1.15226	0.74237
e	0.89223	0.64537	0.75462	0.86345

Table 15.311. The MO to HO intercept geometrical bond parameters of quinoline. E_T is $E_T(atom-atom, msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C-H\ (C_aH)$	C_a	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	76.35	103.65	40.11	1.22423	0.19124
$C-H\ (C_bH)$	C_b	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$N(H)C_a\overset{3e}{=}C_b(H)$	C_a	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	134.85	45.15	59.72	0.74304	0.57165
$(H)C_b\overset{3e}{=}C_{a,b,c,d}(H)$	C_b	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533
$(H)C_b(C_d)C_c\overset{3e}{=}C_b$	C_c	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	-16.61903	134.81	45.19	59.66	0.74430	0.57038
$N(C_c)C_d\overset{3e}{=}C_b$	C_d	-0.85035	-0.54343	-0.28345	0	-153.29292	0.91771	0.82445	-16.50298	-16.31211	135.42	44.58	60.42	0.72743	0.58725
$C_b(H)C_a\overset{3e}{=}N$	C_a	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	128.54	51.46	58.65	0.76572	0.50501
$C_b(H)C_a\overset{3e}{=}N$ $C_b(C_c)C_d\overset{3e}{=}N$	N	-0.54343	-0.54343	0	0		0.93084	0.85503	-15.91261		130.61	49.39	60.97	0.71418	0.55656
$C_b(C_c)C_d\overset{3e}{=}N$	C_d	-0.85035	-0.54343	-0.28345	0	-153.29291	0.91771	0.82445	-16.50297	-16.31211	129.21	50.79	59.38	0.74960	0.52113
$\left((H)C_b\overset{3e}{=}\right)_2 C_c-C_d$	C_c	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	-16.61903	95.01	84.99	44.41	1.25451	0.07066
$N(C_b)C_d-C_c$	C_d	-0.85035	-0.54343	-0.28345	0	-153.29292	0.91771	0.82445	-16.50298	-16.31211	96.31	83.69	45.33	1.23456	0.09061

Table 15.312. The energy parameters (eV) of functional groups of quinoline.

Parameters	$\overset{3e}{C=C}$ Group	CH Group	$C-C$ Group	$\overset{3e}{C=N}$ Group
f_1	0.75	1	1	0.75
n_1	2	1	1	2
n_2	0	0	0	0
n_3	0	0	0	0
C_1	0.5	0.75	0.5	0.5
C_2	0.85252	1	1	0.91140
c_1	1	1	1	1
c_2	0.85252	0.91771	0.85252	0.91140
c_3	0	1	0	0
c_4	3	1	2	3
c_5	0	1	0	0
C_{1o}	0.5	0.75	0.5	0.5
C_{2o}	0.85252	1	1	0.91140
$V_e\ (eV)$	-101.12679	-37.10024	-34.43791	-102.01431
$V_p\ (eV)$	20.69825	13.17125	10.26723	21.41410
$T\ (eV)$	34.31559	11.58941	9.80539	34.65890
$V_m\ (eV)$	-17.15779	-5.79470	-4.90270	-17.32945
$E(AO/HO)\ (eV)$	0	-14.63489	-14.63489	0
$\Delta E_{H_2MO}(AO/HO)\ (eV)$	0	-1.13379	-1.13379	0
$E_T(AO/HO)\ (eV)$	0	-13.50110	-13.50110	0
$E_T(H_2MO)\ (eV)$	-63.27075	-31.63539	-31.63529	-63.27076
$E_T\left(atom-atom,msp^3.AO\right)\ (eV)$	-2.26759	-0.56690	-0.56690	-1.44915
$E_T(MO)\ (eV)$	-65.53833	-32.20226	-32.20226	-64.71988
$\omega\ \left(10^{15}\ rad/s\right)$	49.7272	26.4826	23.6343	43.6311
$E_K\ (eV)$	32.73133	17.43132	15.55648	28.71875
$\bar{E}_D\ (eV)$	-0.35806	-0.26130	-0.25127	-0.33540
$\bar{E}_{Kvib}\ (eV)$	0.19649 [49]	0.35532 Eq. (13.458)	0.12312 [2]	0.19649 [49]
$\bar{E}_{osc}\ (eV)$	-0.25982	-0.08364	-0.18971	-0.23715
$E_{mag}\ (eV)$	0.14803	0.14803	0.14803	0.09457
$E_T(Group)\ (eV)$	-49.54347	-32.28590	-32.39198	-48.82472
$E_{initial}(c_4\ AO/HO)\ (eV)$	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(c_5\ AO/HO)\ (eV)$	0	-13.59844	0	0
$E_D(Group)\ (eV)$	5.63881	3.90454	3.12220	4.92005

Table 15.313. The total bond energies of quinoline calculated using the functional group composition and the energies of Table 15.312 compared to the experimental values [2].].

Formula	Name	$\overset{3e}{C=C}$	CH	$C-C$ Group	$\overset{3e}{C=N}$ Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_9H_7N	Quinbline	8	7	1	2	85.40453	85.48607	0.00178

Table 15.314. The bond angle parameters of quinoline and experimental values [1]. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3B)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3B)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CCC$	2.62936	2.65034	4.5585	-17.17218	20	-17.17218	20	0.79232	0.79232	1	1	1	0.79232	-1.85836				119.40	119.4 (naphthalene)
$\angle CCH$																119.40		120.30	
$\angle C_dNC_a$	2.54147	2.54147	4.3818	-17.43216	22	-17.71560	24	0.78050	0.76801	1	1	1	0.77426	-1.85836				119.10	

ISOQUINOLINE

Isoquinoline has the formula C_9H_7N and comprises the naphthalene molecule with one CH group replaced by a nitrogen atom which gives rise to a $C\overset{3e}{=}N$ functional group. Isoquinoline is also equivalent to quinoline with the nitrogen in the meta rather than the ortho position relative to the benzene ring of the molecule. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups are equivalent to those of naphthalene given in the corresponding section with the aromaticity maintained by the electrons from nitrogen in the $C\overset{3e}{=}N$ group which is also aromatic. The $C-C$ functional group is also equivalent to that of naphthalene. The bonding in isoquinoline can be further considered as a linear combination of the naphthalene and pyridine groups wherein the $C\overset{3e}{=}N$ group is equivalent to that of pyridine, pyrimidine, pyrazine, and quinoline as given in the corresponding sections.

The symbols of the functional groups of isoquinoline are given in Table 15.315. The corresponding designation of the structure is shown in Figure 73. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of isoquinoline are given in Tables 15.316, 15.317, and 15.318, respectively. The total energy of isoquinoline given in Table 15.319 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.318 corresponding to functional-group composition of the molecule. The bond angle parameters of isoquinoline determined using Eqs. (15.79-15.108) are given in Table 15.320.

Table 15.315. The symbols of functional groups of isoquinoline.

Functional Group	Group Symbol
CC (aromatic bond)	$C\overset{3e}{=}C$
CH (aromatic)	CH
C_b-C_b (bridging bond)	$C-C$
$C_{a,d}\overset{3e}{=}N$	$C\overset{3e}{=}N$

Table 15.316. The geometrical bond parameters of isoquinoline and experimental values [1].

Parameter	$\overset{3e}{C=C}$ Group	CH Group	$C-C$ Group	$\overset{3e}{C=N}$ Group
$a\ (a_0)$	1.47348	1.60061	1.75607	1.47169
$c'\ (a_0)$	1.31468	1.03299	1.32517	1.27073
Bond Length $2c'$ $(Å)$	1.39140	1.09327	1.40250	1.34489
Exp. Bond Length $(Å)$	1.40 (avg.) (naphthalene)	1.101 (benzene)	1.42 (naphthalene)	1.340 (pyridine)
$b,c\ (a_0)$	0.66540	1.22265	1.15226	0.74237
e	0.89223	0.64537	0.75462	0.86345

Table 15.317. The MO to HO intercept geometrical bond parameters of isoquinoline. E_T is $E_T(atom-atom, msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C-H\ (C_aH)$	C_a	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	76.35	103.65	40.11	1.22423	0.19124
$C-H\ (C_bH)$	C_b	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	76.35	103.65	40.11	1.22423	0.19124
$C-H\ (C_cH)$	C_c	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$N(H)C_a\overset{3e}{=}C_d$ $N(H)C_b\overset{3e}{=}C_c$	C_a C_b	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	134.85	45.15	59.72	0.74304	0.57165
$(H)C_c\overset{3e}{=}C_{b,c,d}(H)$	C_c	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533
$(H)C_c(C_d)C_d\overset{3e}{=}C_{a,c}$	C_d	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	-16.61903	134.81	45.19	59.66	0.74430	0.57038
$C_d(H)C_a\overset{3e}{=}N$ $C_c(H)C_b\overset{3e}{=}N$	C_a C_b	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	128.54	51.46	58.65	0.76572	0.50501
$C_d(H)C_a\overset{3e}{=}N$ $C_c(H)C_b\overset{3e}{=}N$	N	-0.54343	-0.54343	0	0		0.93084	0.85503	-15.91261		130.61	49.39	60.97	0.71418	0.55656
$C_{a,c}(C_c)C_d-C_d$	C_d	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	-16.61903	95.01	84.99	44.41	1.25451	0.07066

Table 15.318. The energy parameters (eV) of functional groups of isoquinoline.

Parameters	$\overset{3e}{C=C}$ Group	CH Group	$C-C$ Group	$\overset{3e}{C=N}$ Group
f_1	0.75	1	1	0.75
n_1	2	1	1	2
n_2	0	0	0	0
n_3	0	0	0	0
C_1	0.5	0.75	0.5	0.5
C_2	0.85252	1	1	0.91140
c_1	1	1	1	1
c_2	0.85252	0.91771	0.85252	0.91140
c_3	0	1	0	0
c_4	3	1	2	3
c_5	0	1	0	0
C_{1o}	0.5	0.75	0.5	0.5
C_{2o}	0.85252	1	1	0.91140
$V_e\ (eV)$	-101.12679	-37.10024	-34.43791	-102.01431
$V_p\ (eV)$	20.69825	13.17125	10.26723	21.41410
$T\ (eV)$	34.31559	11.58941	9.80539	34.65890
$V_m\ (eV)$	-17.15779	-5.79470	-4.90270	-17.32945
$E(AO/HO)\ (eV)$	0	-14.63489	-14.63489	0
$\Delta E_{H_2MO}(AO/HO)\ (eV)$	0	-1.13379	-1.13379	0
$E_T(AO/HO)\ (eV)$	0	-13.50110	-13.50110	0
$E_T(H_2MO)\ (eV)$	-63.27075	-31.63539	-31.63529	-63.27076
$E_T(atom-atom,msp^3.AO)\ (eV)$	-2.26759	-0.56690	-0.56690	-1.44915
$E_T(MO)\ (eV)$	-65.53833	-32.20226	-32.20226	-64.71988
$\omega\ (10^{15}\ rad/s)$	49.7272	26.4826	23.6343	43.6311
$E_K\ (eV)$	32.73133	17.43132	15.55648	28.71875
$\bar{E}_D\ (eV)$	-0.35806	-0.26130	-0.25127	-0.33540
$\bar{E}_{Kvib}\ (eV)$	0.19649 [49]	0.35532 Eq. (13.458)	0.12312 [2]	0.19649 [49]
$\bar{E}_{osc}\ (eV)$	-0.25982	-0.08364	-0.18971	-0.23715
$E_{mag}\ (eV)$	0.14803	0.14803	0.14803	0.09457
$E_T(Group)\ (eV)$	-49.54347	-32.28590	-32.39198	-48.82472
$E_{initial}(c_4\ AO/HO)\ (eV)$	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(c_5\ AO/HO)\ (eV)$	0	-13.59844	0	0
$E_D(Group)\ (eV)$	5.63881	3.90454	3.12220	4.92005

Table 15.319. The total bond energies of isoquinoline calculated using the functional group composition and the energies of Table 15.318 compared to the experimental values [2].].

Formula	Name	$\overset{3e}{C=C}$	CH	$C-C$ Group	$\overset{3e}{C=N}$ Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_9H_7N	Isoquinoline	8	7	1	2	85.40453	85.44358	0.00046

Table 15.320. The bond angle parameters of isoquinoline and experimental values [1]. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3B)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3B)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CCC$	2.62936	2.65034	4.5585	-17.17218	20	-17.17218	20	0.79232	0.79232	1	1	1	0.79232	-1.85836				119.40	119.4 (naphthalene)
$\angle CCH$																119.40		120.30	
$\angle C_aNC_b$	2.54147	2.54147	4.3818	-17.43216	22	-17.71560	24	0.78050	0.76801	1	1	1	0.77426	-1.85836				119.10	

INDOLE

Indole having the formula C_8H_7N comprises a phenyl moiety with a conjugated five-membered ring which comprises pyrrole except that one of the double bonds is part of the aromatic ring. The structure is shown in Figure. 74. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups of the phenyl moiety are equivalent to those of benzene given in the Aromatic and Heterocyclic Compounds section. The CH, NH, and $C_d=C_e$ groups of the pyrrole-type ring are equivalent to the corresponding groups of pyrrole, furan, and thiophene where present as given in the corresponding sections. The C_b-C_d single bond of aryl carbon to the $C_d=C_e$ bond is also a functional group. This group is equivalent to the $C-C(O)$ group of benzoic acids with regard to $\Delta E_{H_2MO}(AO/HO)$ in Eq. (15.42) and $E_T(atom-atom,msp^3.AO)$ in Eq. (15.52) both being $-1.29147\ eV$. This energy is a linear combination of $\frac{-1.13379\ eV}{2}$, $E_T(atom-atom,msp^3.AO)$ of the $C-H$ group that the C_b-C_d and $C-C(O)$ groups replace, and that of an independent $C2sp^3$ HO, $-0.72457\ eV$ (Eq. (14.151)). However, as in the case of pyrrole, the indole hybridization term c_2 is the aromatic $c_2(benzeneC2sp^3HO)=0.85252$ to match the aryl $C2sp^3$ HO, and the energy terms corresponding to oscillation in the transition state correspond to indole.

As in the case of pyrrole, the $C-N-C$-bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with $n_1=2$ in Eqs. (15.42) and (15.52). The hybridization factor $c_2(arylC2sp^3HO\ to\ N)=0.84665$ (Eq. (15.152)) matches the aromatic character of the $C2sp^3$ HOs to the N atom of the NH group, and C_2 and C_{2o} in Eqs. (15.42) and (15.52) become that of benzene given by Eq. (15.143), $C_2(benzeneC2sp^3HO)=0.85252$. Furthermore, $\Delta E_{H_2MO}(AO/HO)$ in Eq. (15.42) and $E_T(atom-atom,msp^3.AO)$ in Eq. (15.52) are both $-2.42526\ eV$ which is a linear combination of $\frac{-1.13379\ eV}{2}$, $E_T(atom-atom,msp^3.AO)$ of the $C-H$ group that the C_c-N bond replaces, and $-1.85836\ eV$ (Eq. (14.513)) which is equivalent to the corresponding component of the $C-N-C$-bond of pyrrole.

The symbols of the functional groups of indole are given in Table 15.321. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of indole are given in Tables 15.322, 15.323, and 15.324, respectively. The total energy of indole given in Table 15.325 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.324 corresponding to functional-group composition of the molecule. The bond angle parameters of indole determined using Eqs. (15.79-15.108) are given in Table 15.326.

Table 15.321. The symbols of functional groups of indole.

Functional Group	Group Symbol
CC (aromatic bond)	$C\overset{3e}{=}C$
CH (aromatic)	CH (i)
$C_d = C_e$ double bond	$C=C$
$C_b - C_d$	$C-C$
CH	CH (ii)
$C_c - N - C_e$	$C-N-C$
NH group	NH

Table 15.322. The geometrical bond parameters of indole and experimental values [1].

Parameter	$C\overset{3e}{=}C$ Group	$C'H$ (i) Group	$C=C$ Group	$C'H$ (ii) Group	$C-C$ Group	$C-N-C$ Group	NH Group
$a\ (a_0)$	1.47348	1.60061	1.45103	1.53380	1.81395	1.44394	1.24428
$c'\ (a_0)$	1.31468	1.03299	1.30463	1.01120	1.34683	1.30144	0.94134
Bond Length $2c'\ (\text{Å})$	1.39140	1.09327	1.38076	1.07021	1.42542	1.37738	0.996270
Exp. Bond Length (Å)	1.399 (benzene)	1.101 (benzene)	1.382 (pyrrole)	1.076 (pyrrole	1.417 (pyrrole)	1.370 (pyrrole)	0.996 (pyrrole)
$b,c\ (a_0)$	0.66540	1.22265	0.63517	1.15326	1.21510	0.62548	0.81370
e	0.89223	0.64537	0.89910	0.65928	0.74248	0.90131	0.75653

Table 15.323. The MO to HO intercept geometrical bond parameters of indole. R_1 is an alkyl group and R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C'-H\ (C'_aH)$	C'_a	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$C'_a\overset{3e}{=}HC'_a\overset{3e}{=}C'_{a,b,c}$	C'_a	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533
$C'_a\overset{3e}{=}(C'_d)C'_b\overset{3e}{=}C'_c$ $C'_c\overset{3e}{=}(C'_d)C'_b\overset{3e}{=}C'_a$	C'_b	-0.85035	-0.64574	-0.85035	0	-153.96212	0.91771	0.79232	-17.17218	-16.98132	134.09	45.91	58.79	0.76344	0.55124
$C'_a\overset{3e}{=}C'_c(N)C'_b$ $C'_b\overset{3e}{=}C'_c(N)C'_a$	C'_c	-0.60631	-0.85035	-0.85035	0	-153.92270	0.91771	0.79414	-17.13276	-16.94190	134.16	45.84	58.89	0.76140	0.55328
$C'_a(H)C'_b-C'_d(H)C'_e$	C'_b	-0.85035	-0.85035	-0.64574	0	-153.96212	0.91771	0.79232	-17.17218	-16.98132	87.89	92.11	40.66	1.37597	0.02914
$C'_a(H)C'_b-C'_d(H)C'_e$	C'_d	-0.64574	-1.13379	0	0	-153.39522	0.91771	0.81937	-16.60528	-16.41442	90.51	89.49	42.40	1.33953	0.00729
$C'_b(H)C'_d=C'_eN$	C'_d	-0.64574	-1.13379	0	0	-153.39522	0.91771	0.81937	-16.60528	-16.41442	137.29	42.71	61.04	0.70255	0.60208
$C'_b(H)C'_d=C'_eN$	C'_e	-1.13379	-0.60631	0	0	-153.35580	0.91771	0.82132	-16.56586	-16.37500	137.37	42.63	61.14	0.70038	0.60425
$C'_dC'_e-NC'_e$	C'_e	-1.13379	-0.60631	0	0	-153.35580	0.91771	0.82132	-16.56586	-16.37500	138.03	41.97	61.42	0.69080	0.61064
$C'_dC'_e-NC'_c$ $C'_aC'_c-NC'_e$	N	-0.60631	-0.60631	0	0		0.93084	0.84833	-16.03838		139.04	40.96	62.76	0.66083	0.64061
$N-H\ (NH)$	N	-0.60631	-0.60631	0	0		0.93084	0.84833	-16.03838		119.52	60.48	65.13	0.52338	0.41796
$C'_aC'_c-NC'_e$	C'_c	-0.85035	-0.85035	-0.60631	0	-153.92269	0.91771	0.79414	-17.13276	-16.94189	136.97	43.03	60.05	0.72095	0.58048

Table 15.324. The energy parameters (eV) of functional groups of indole.

Parameters	$\overset{3e}{C=C}$ Group	CH (i) Group	$C=C$ Group	$C-C$ Group	CH (ii) Group	$C-N-C$ Group	NH Group
f_1	0.75	1	1	1	1	1	1
n_1	2	1	2	1	1	2	1
n_2	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0
C_1	0.5	0.75	0.5	0.5	0.75	0.5	0.75
C_2	0.85252	1	0.85252	1	1	0.85252	0.93613
c_1	1	1	1	1	1	1	0.75
c_2	0.85252	0.91771	0.85252	0.85252	0.91771	0.84665	0.92171
c_3	0	1	0	0	1	0	1
c_4	3	1	4	2	1	4	1
c_5	0	1	0	0	1	0	1
C_{1o}	0.5	0.75	0.5	0.5	0.75	0.5	0.75
C_{2o}	0.85252	1	0.85252	1	1	0.85252	1
$V_e\ (eV)$	-101.12679	-37.10024	-104.37986	-32.93291	-39.09538	-104.73877	-39.48897
$V_p\ (eV)$	20.69825	13.17125	20.85777	10.10210	13.45505	20.90891	14.45367
$T\ (eV)$	34.31559	11.58941	35.96751	9.07768	12.74462	36.26840	15.86820
$V_m\ (eV)$	-17.15779	-5.79470	-17.98376	-4.53884	-6.37231	-18.13420	-7.93410
$E(_{AO/HO})\ (eV)$	0	-14.63489	0	-14.63489	-14.63489	0	-14.53414
$\Delta E_{H_2MO}(_{AO/HO})\ (eV)$	0	-1.13379	-2.26759	-1.29147	-2.26758	-2.42526	0
$E_T(_{AO/HO})\ (eV)$	0	-13.50110	2.26759	-13.34342	-12.36731	2.42526	-14.53414
$E_T(_{H_2MO})\ (eV)$	-63.27075	-31.63539	-63.27075	-31.63539	-31.63533	-63.27040	-31.63534
$E_T(atom-atom,msp^3.AO)\ (eV)$	-2.26759	-0.56690	-2.26759	-1.29147	0	-2.42526	0
$E_T(_{MO})\ (eV)$	-65.53833	-32.20226	-65.53833	-32.92684	-31.63537	-65.69600	-31.63537
$\omega\ (10^{15}\ rad/s)$	49.7272	26.4826	15.4421	21.8249	28.9084	54.5632	48.7771
$E_K\ (eV)$	32.73133	17.43132	10.16428	14.36554	19.02803	35.91442	32.10594
$\bar{E}_D\ (eV)$	-0.35806	-0.26130	-0.20668	-0.24690	-0.27301	-0.38945	-0.35462
$\bar{E}_{Kvib}\ (eV)$	0.19649 [49]	0.35532 Eq. (13.458)	0.17897 [6]	0.12312 [2]	0.39427 [56]	0.11159 [12]	0.40696 [24]
$\bar{E}_{osc}\ (eV)$	-0.25982	-0.08364	-0.11720	-0.18534	-0.07587	-0.33365	-0.15115
$E_{mag}\ (eV)$	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(_{Group})\ (eV)$	-49.54347	-32.28590	-65.77272	-33.11218	-31.71124	-66.36330	-31.78651
$E_{initial}(_{c_4\ AO/HO})\ (eV)$	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.53414
$E_{initial}(_{c_5\ AO/HO})\ (eV)$	0	-13.59844	0	0	-13.59844	0	-13.59844
$E_D(_{Group})\ (eV)$	5.63881	3.90454	7.23317	3.84240	3.32988	7.82374	3.51208

Table 15.325. The total bond energies of indole calculated using the functional group composition and the energies of Table 15.324 compared to the experimental values [2].

Formula	Name	$\overset{3e}{C=C}$	CH (i)	$C=C$	$C-C$	CH (ii)	$C-N-C$	NH	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_8H_7N	Indole	6	4	1	1	2	1	1	78.52215	78.514	-0.00010

Table 15.326. The bond angle parameters of indole and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom, msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3B)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3B)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CCC$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	20	-17.17218	20	0.79232	0.79232	1	1	1	0.79232	-1.85836				120.19	120 [50-52] (benzene)
$\angle CCH$ (aromatic)																120.19		119.91	120 [50-52] (benzene)

ADENINE

Adenine having the formula $C_5H_5N_5$ comprises a pyrimidine moiety with an aniline group and a conjugated five-membered ring which comprises imidazole except that one of the double bonds is part of the aromatic ring. The structure is shown in Figure. 75. The aromatic $C\overset{3e}{=}C$, $C-H$, and $C\overset{3e}{=}N$ functional groups of the pyrimidine moiety are equivalent to those of pyrimidine as given in the corresponding section. The NH_2 and C_a-N_a functional groups of the aniline moiety are equivalent to those of aniline as given in the corresponding section. The CH, NH, C_d-N_e, and $N_e=C_e$ groups of the imidazole-type ring are equivalent to the corresponding groups of imidazole as given in the corresponding section. The $C-N-C$ functional group of the imidazole-type ring is equivalent to the corresponding group of indole having the same structure with the $C-N-C$ group bonding to aryl and alkenyl groups.

The symbols of the functional groups of adenine are given in Table 15.327. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of adenine are given in Tables 15.328, 15.329, and 15.330, respectively. The total energy of adenine given in Table 15.332 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.330 corresponding to functional-group composition of the molecule. The bond angle parameters of adenine determined using Eqs. (15.79-15.108) are given in Table 15.332.

Table 15.327. The symbols of functional groups of adenine.

Functional Group	Group Symbol
CC (aromatic bond)	$C\overset{3e}{=}C$
CH (aromatic)	CH (i)
$C_{b,c}\overset{3e}{=}N_c$ $\quad C_{a,b}\overset{3e}{=}N_b$	$C\overset{3e}{=}N$
C_a-N_a	$C-N$ (a)
NH_2 group	NH_2
$N_e=C_e$ double bond	$N=C$
C_d-N_e	$C-N$ (b)
N_dH group	NH
CH	CH (ii)
$C_c-N_d-C_e$	$C-N-C$

Table 15.328. The geometrical bond parameters of adenine and experimental values [1].

Parameter	$\overset{3e}{C=C}$ Group	CH (i) Group	$\overset{3e}{C=N}$ Group	$C-N$ (a) Group	NH_2 Group	$N=C$ Group	$C-N$ (b) Group	NH Group	CH (ii) Group	$C-N-C$ Group
$a\ (a_0)$	1.47348	1.60061	1.47169	1.81158	1.24428	1.44926	1.82450	1.24428	1.53380	1.44394
$c'\ (a_0)$	1.31468	1.03299	1.27073	1.34595	0.94134	1.30383	1.35074	0.94134	1.01120	1.30144
Bond Length $2c'$ ($Å$)	1.39140	1.09327	1.34489	1.42449	0.99627	1.37991	1.42956	0.996270	1.07021	1.37738
Exp. Bond Length ($Å$)	1.393 (pyrimidine)	1.084 (pyridine)	1.340 (pyrimidine)	1.431 (aniline)	0.998 (aniline)			0.996 (pyrrole)	1.076 (pyrrole)	1.370 (pyrrole)
$b,c\ (a_0)$	0.66540	1.22265	0.74237	1.21254	0.81370	0.63276	1.22650	0.81370	1.15326	0.62548
e	0.89223	0.64537	0.86345	0.74297	0.75653	0.89965	0.74033	0.75653	0.65928	0.90131

Table 15.329. The MO to HO intercept geometrical bond parameters of adenine. R_1 is an alkyl group and R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C_d(N_b)C_aN_aH-H$	N_a	-0.56690	0	0	0		0.93084	0.88392	-15.39265		121.74	58.26	67.49	0.47634	0.46500
$C_d(N_b)C_a-N_aH_2$	C_a	-0.56690	-0.54343	-0.85035	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	89.90	90.10	41.95	1.34737	0.00142
$C_d(N_b)C_a-N_aH_2$	N_a	-0.56690	0	0	0		0.93084	0.88392	-15.39265		96.32	83.68	46.43	1.24859	0.09736
$C-H\ (C_bH)$	C_b	-0.54343	-0.54343	-0.56690	0	-153.26945	0.91771	0.82562	-16.47951	-16.28864	78.27	101.73	41.39	1.20084	0.16785
$C-H\ (C_cH)$	C_c	-0.92918	-0.60631	0	0	-153.15119	0.91771	0.83159	-16.36125	-16.17038	79.01	100.99	41.89	1.19159	0.15860
$N-H\ (N_dH)$	N	-0.60631	-0.60631	0	0		0.93084	0.84833	-16.03838		119.52	60.48	65.13	0.52338	0.41796
$C_d(NH_2)C_a\overset{3e}{=}N_bC_b$	C_a	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	128.54	51.46	58.65	0.76572	0.50501
$C_d(NH_2)C_a\overset{3e}{=}N_bC_b$ $N_bC_b\overset{3e}{=}N_cC_c$	N_b N_c	-0.54343	-0.54343	0	0		0.93084	0.85503	-15.91261		130.61	49.39	60.97	0.71418	0.55656
$N_bC_b\overset{3e}{=}N_cC_c$ $C_aN_b\overset{3e}{=}C_bN_c$	C_b	-0.54343	-0.54343	-0.56690	0	-153.26945	0.91771	0.82562	-16.47951	-16.28865	129.26	50.74	59.44	0.74824	0.52249
$C_d(N_dH)C_c\overset{3e}{=}N_cC_b$	C_c	-0.85035	-0.54343	-0.60631	0	-153.61578	0.91771	0.80863	-16.82584	-16.63498	128.45	51.55	58.55	0.76792	0.50281
$N_b(N_aH_2)C_a\overset{3e}{=}C_d(N_e)C_e$	C_a	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	134.85	45.15	59.72	0.74304	0.57165
$N_b(N_aH_2)C_a\overset{3e}{=}C_d(N_e)C_e$ $C_a(N_e)C_d\overset{3e}{=}C_e(N_dH)N_c$	C_d	-0.85035	-0.85035	-0.46459	0	-153.78097	0.91771	0.80076	-16.99103	-16.80017	134.44	45.56	59.22	0.75398	0.56071
$C_a(N_e)C_d\overset{3e}{=}C_e(N_dH)N_c$	C_e	-0.85035	-0.54343	-0.60631	0	-153.61578	0.91771	0.80863	-16.82584	-16.63498	134.77	45.23	59.62	0.74516	0.56952
$C_d(N_c)C_e-N_dH$	C_e	-0.85035	-0.54343	-0.60631	0	-153.61578	0.91771	0.80863	-16.82584	-16.63498	137.54	42.46	60.78	0.70488	0.59656
$C_c(H)N_d-C_e(N_c)C_d$ $N_c(H)C_c-N_d(H)C_e$	N_d	-0.60631	-0.60631	0	0		0.93084	0.84833	-16.03838		139.04	40.96	62.76	0.66083	0.64061
$N_c(H)C_c-N_d(H)C_e$	C_c	-0.60631	-0.92918	0	0	-153.15119	0.91771	0.83159	-16.36125	-16.17039	138.42	41.58	61.93	0.67940	0.62203
$C_dN_e=C_f(H)N_dH$	C_f	-0.92918	-0.60631	0	0	-153.15119	0.91771	0.83159	-16.36125	-16.17039	137.93	42.07	61.72	0.68657	0.61726
$C_dN_e=C_f(H)N_dH$	N_e	-0.92918	-0.46459	0	0		0.93084	0.83885	-16.21952		138.20	41.80	62.08	0.67849	0.62534
$C_a(C_e)C_d-N_eC_f$	N_e	-0.46459	-0.92918	0	0		0.93084	0.83885	-16.21952		91.32	88.68	43.14	1.33135	0.01939
$C_a(C_e)C_d-N_eC_f$	C_d	-0.46459	-0.85035	-0.85035	0	-153.78097	0.91771	0.80076	-16.99103	-16.80017	87.71	92.29	40.72	1.38280	0.03206

Table 15.330. The energy parameters (eV) of functional groups of adenine.

Parameters	$\overset{3e}{C=C}$ Group	CH (i) Group	$\overset{3e}{C=N}$ Group	$C-N$ (a) Group	NH_2 Group	$N=C$ Group	$C-N$ (b) Group	NH Group	CH (ii) Group	$C-N-C$ Group
f_1	0.75	1	0.75	1	1	1	1	1	1	1
n_1	2	1	2	1	2	2	1	1	1	2
n_2	0	0	0	0	0	0	0	0	0	0
n_3	0	0	0	0	1	0	0	0	0	0
C_1	0.5	0.75	0.5	0.5	0.75	0.5	0.5	0.75	0.75	0.5
C_2	0.85252	1	0.91140	1	0.93613	0.85252	1	0.93613	1	0.85252
c_1	1	1	1	1	0.75	1	1	0.75	1	1
c_2	0.85252	0.91771	0.91140	0.84665	0.92171	0.84665	0.84665	0.92171	0.91771	0.84665
c_3	0	1	0	0	0	0	0	1	1	0
c_4	3	1	3	2	1	4	2	1	1	4
c_5	0	1	0	0	2	0	0	1	1	0
C_{1o}	0.5	0.75	0.5	0.5	1.5	0.5	0.5	0.75	0.75	0.5
C_{2o}	0.85252	1	0.91140	1	1	0.85252	1	1	1	0.85252
$V_e\ (eV)$	-101.12679	-37.10024	-102.01431	-32.76465	-78.97795	-103.92756	-32.44864	-39.48897	-39.09538	-104.73877
$V_p\ (eV)$	20.69825	13.17125	21.41410	10.10870	28.90735	20.87050	10.07285	14.45367	13.45505	20.90891
$T\ (eV)$	34.31559	11.58941	34.65890	9.04312	31.73641	35.85539	8.89248	15.86820	12.74462	36.26840
$V_m\ (eV)$	-17.15779	-5.79470	-17.32945	-4.52156	-15.86820	-17.92770	-4.44624	-7.93410	-6.37231	-18.13420
$E(_{AO/HO})\ (eV)$	0	-14.63489	0	-14.63489	-14.53414	0	-14.63489	-14.53414	-14.63489	0
$\Delta E_{H_2MO}(_{AO/HO})\ (eV)$	0	-1.13379	0	-1.13379	0	-1.85836	-0.92918	0	-2.26758	-2.42526
$E_T(_{AO/HO})\ (eV)$	0	-13.50110	0	-13.50110	-14.53414	1.85836	-13.70571	-14.53414	-12.36731	2.42526
$E(_{n_3,AO/HO})\ (eV)$	0	0	0	0	-14.53414	0	0	0	0	0
$E_T(_{H_2MO})\ (eV)$	-63.27075	-31.63539	-63.27076	-31.63549	-48.73654	-63.27100	-31.63527	-31.63534	-31.63533	-63.27040
$E_T(atom-atom,msp^3.AO)\ (eV)$	-2.26759	-0.56690	-1.44915	-1.13379	0	-1.85836	-0.92918	0	0	-2.42526
$E_T(_{MO})\ (eV)$	-65.53833	-32.20226	-64.71988	-32.76916	-48.73660	-65.12910	-32.56455	-31.63537	-31.63537	-65.69600
$\omega\ (10^{15}\ rad/s)$	49.7272	26.4826	43.6311	11.9890	68.9812	15.4704	21.5213	48.7771	28.9084	54.5632
$E_K\ (eV)$	32.73133	17.43132	28.71875	7.89138	45.40465	10.18290	14.16571	32.10594	19.02803	35.91442
$\bar{E}_D\ (eV)$	-0.35806	-0.26130	-0.33540	-0.18211	-0.42172	-0.20558	-0.24248	-0.35462	-0.27301	-0.38945
$\bar{E}_{Kvib}\ (eV)$	0.19649 [49]	0.35532 Eq. (13.458)	0.19649 [49]	0.15498 [54]	0.40929 [22]	0.20768 [58]	0.12944 [23]	0.40696 [24]	0.39427 [56]	0.11159 [12]
$\bar{E}_{osc}\ (eV)$	-0.25982	-0.08364	-0.23715	-0.10462	-0.21708	-0.10174	-0.17775	-0.15115	-0.07587	-0.33365
$E_{mag}\ (eV)$	0.14803	0.14803	0.09457	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(_{Group})\ (eV)$	-49.54347	-32.28590	-48.82472	-32.87379	-49.17075	-65.33259	-32.74230	-31.78651	-31.71124	-66.36330
$E_{initial}(_{c_4\ AO/HO})\ (eV)$	-14.63489	-14.63489	-14.63489	-14.63489	-14.53414	-14.63489	-14.63489	-14.53414	-14.63489	-14.63489
$E_{initial}(_{c_5\ AO/HO})\ (eV)$	0	-13.59844	0	0	-13.59844	0	0	-13.59844	-13.59844	0
$E_D(_{Group})\ (eV)$	5.63881	3.90454	4.92005	3.60401	7.43973	6.79303	3.47253	3.51208	3.32988	7.82374

Table 15.331. The total bond energies of adenine calculated using the functional group composition and the energies of Table 15.330 compared to the experimental values [2].

Formula	Name	$\overset{3e}{C=C}$	CH (i)	$\overset{3e}{C=N}$ Group	$C-N$ (a) Group	NH_2 Group	$N=C$	$C-N$ (b)	NH	CH (ii)	$C-N-C$	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_5H_5N_5$	Adenine	2	1	4	1	1	1	1	1	1	1	70.83735	70.79811	-0.00055

Table 15.332. The bond angle parameters of adenine and experimental values [61]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3B)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3B)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HNH$	1.88268	1.88268	3.1559	-14.53414	N	H	H	0.93613 Eq. (13.248))	1	1	1	0.75	1.06823	0				113.89	113.9 [1] (aniline)
$\angle HNC'_a$	1.88268	2.69190	4.0497	-14.53414	N	-15.95955	6	0.84665 (Eq. (15.152))	0.86284 (Eq. (15.64))	0.75	1	0.75	1.01912	0				123.60	118
$\angle H_bC_bN_b$ $\angle H_bC_bN_c$	2.06598	2.54147	3.9497	-14.82575	1	-14.53414	N	0.91771	0.91140 Eq. (15.116))	0.75	1	0.75	0.99312	0				117.65	115 116
$\angle H_eC_eN_e$	2.02241	2.60766	4.0661	-16.36125	10	-14.53414	N	0.83159	0.84665 Eq. (15.152))	0.75	1	0.75	1.01811	0				122.35	126
$\angle H_eC_eN_d$																122.35	112.64	125.02	119
$\angle H_dN_dC_e$ $\angle H_dN_dC_e$	1.88268	2.60287	4.0497	-14.53414	N	-15.95955	6	0.84665 (Eq. (15.152))	0.86284 (Eq. (15.64))	0.75	1	0.75	1.10912	0				128.35	127
$\angle N_eC_eN_d$	2.60766	2.60287	4.3359	-16.21952	8	-16.03838	7	0.83885	0.84833	1	1	1	0.84359	-1.44915				112.64	114.4
$\angle N_cC_eN_d$	2.54147	2.60287	4.6260	-14.53414	N	-14.53414	N	0.91140 Eq. (15.116))	0.84665 Eq. (15.152))	1	1	1	0.87902	-1.44915				128.11	127.8
$\angle N_bC_bN_c$	2.54147	2.54147	4.5826	-15.55033	3	-15.55033	3	0.87495	0.87495	1	1	1	0.87495	-1.44915				128.73	128.9
$\angle N_bC_aN_a$	2.54147	2.69190	4.5826	-15.91261	5	-15.39265	2	0.85503	0.88392	1	1	1	0.86947	-1.44915				122.22	119.7
$\angle N_eC_dC_c$	2.70148	2.62936	4.3818	-14.53414	N	-15.95955 C_c	6	0.84665 (Eq. (15.152))	0.85252	1	1	1	0.84958	-1.44915				110.56	110.4
$\angle N_dC_cC_d$	2.60287	2.62936	4.1952	-14.53414	N	-16.99103 C_d	16	0.84665 (Eq. (15.152))	0.80076	1	1	1	0.82371	-1.44915				106.60	105.9
$\angle N_cC_cC_d$	2.54147	2.62936	4.4721	-14.53414	N	-16.99103 C_d	16	0.91140 Eq. (15.116))	0.80076	1	1	1	0.85608	-1.44915				119.73	126.4
$\angle N_bC_aC_d$	2.54147	2.62936	4.4721	-14.53414	N	-16.99103 C_d	16	0.91140 Eq. (15.116))	0.80076	1	1	1	0.85608	-1.44915				119.73	118.2
$\angle N_aC_aC_d$	2.69190	2.62936	4.5607	-14.53414	N	-16.52644 C_d	12	0.91140 Eq. (15.116))	0.82327	1	1	1	0.86734	-1.44915				117.97	122.1
$\angle N_eC_dC_a$	2.70148	2.62936	4.8990	-14.53414	N	-14.82575 C_a	1	0.91140 Eq. (15.116))	0.91771	1	1	1	0.91456	-1.44915				133.55	132.8
$\angle C_dN_eC_e$	2.70148	2.60766	4.2661	-17.92022	28	-17.92022	28	0.75924	0.75924	1	1	1	0.75924	-1.85836				106.93	103.3
$\angle C'_cN_dC'_c$	2.60287	2.60287	4.2661	-17.75502	25	-17.75502	25	0.76631	0.76631	1	1	1	0.76631	-1.85836				110.07	106.1
$\angle C_bN_cC_c$	2.54147	2.54147	4.3589	-17.40869	21	-17.75502	25	0.78155	0.76631	1	1	1	0.77393	-1.85836				118.09	111.3
$\angle C_aN_bC_b$	2.54147	2.54147	4.3704	-17.71560	24	-17.40869	21	0.76801	0.78155	1	1	1	0.77478	-1.85836				118.59	118.6
$\angle C_aC_dC_c$	2.62936	2.62936	4.4721	-17.71560	24	-17.14871	19	0.76801	0.79340	1	1	1	0.78071	-1.85836				116.52	116.7

While the claimed invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one of ordinary skill in the art that various changes and modifications can be made to the claimed invention without departing from the spirit and scope thereof.